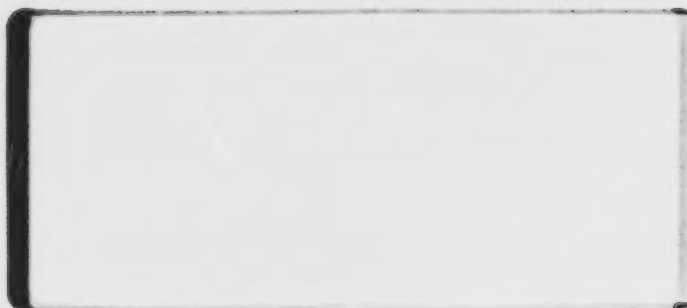


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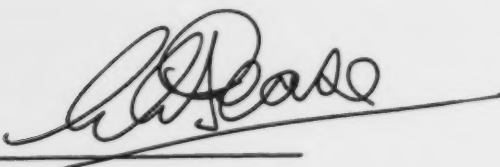


GULF CANADA LIMITED

**RESEARCH AND DEVELOPMENT DEPARTMENT
SHERIDAN PARK, ONTARIO, CANADA**

THE USE OF ALKALINE WATERFLOODING AS
AN ENHANCED RECOVERY PROCESS FOR
HEAVY OILS

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OBJECTIVE

The overall objective of this project is to study the feasibility of alkaline waterflooding of a Saskatchewan heavy oil reservoir and to investigate the controlling process mechanisms.

During alkaline flooding, several mechanisms have been identified as having the potential for increasing oil production in a secondary or tertiary recovery mode. This project endeavours to examine the role and potential of alkaline additives in heavy oil recovery, and thereby provides a basis for the optimization of such processes.

The specific areas of study are:

- . Screening of alkaline waterflood additives (by type and concentration) using interfacial tension (IFT) reduction and wettability modification criteria.
- . Process evaluation by estimation of oil recovery improvement vs. waterflooding using core displacement tests.
- . Study of improved mobility and sweep efficiency due to in situ emulsification and entrapment mechanisms.
- . Rock reactivity study and the possible impact on caustic consumption.

JUSTIFICATION

Canada's Heavy Oil deposits constitute a large (25 billion barrels of Oil In Place estimated for Saskatchewan alone) unexploited resource which poses unique recovery problems.

The recovery process adopted depends largely on reservoir properties such as fluids saturation and distribution, pay thickness, porosity, permeability, burial depth, heterogeneity, mineralogy, pay zone confinement by natural barriers, dip and the logistics of applying a certain process.

Whilst thermal methods are popular and provide the necessary mobility improvement and reservoir energy, reservoir heterogeneity can hinder these processes by channelling the injected air or steam out of the pattern. Small pay thickness could result in high heat losses to over and underburden rock. Reservoirs falling into this category become prime candidates for non-thermal recovery processes such as chemical floods with caustic waterflooding providing an attractive alternative where improvements in oil recovery of approximately 30% over waterfloods have been reported in the literature.

The primary mechanisms by which caustic waterflooding can lead to significant improvements in the recovery of certain crude oils are believed to be wettability changes and reduction of oil-water interfacial tension (IFT). By reacting with certain organic acids present in the crude oil, caustic solutions can generate surfactants (or soaps) in situ, which concentrate at the oil/water interfaces and reduce the IFT, resulting in crude oil emulsification and wettability changes. In high viscosity crudes, in situ production of emulsions may tend to inhibit viscous fingering or water channelling by reducing the mobility ratio between reservoir and injected fluids resulting in improved volumetric sweep efficiency.

Whilst caustic waterflooding of light oil reservoirs is a recognized EOR process, the dominant mechanism in caustic - heavy oil processes have not been well defined. In order to make a chemical flood of this type cost effective and to provide guidelines for process optimization, it is essential that the recovery mechanism be better defined. In particular, reduction of IFT to levels required for in situ emulsification requires considerably lower caustic concentrations than for activation of wettability reversal mechanisms. Since in situ emulsification may be responsible for improved sweep efficiency in heavy oil applications, optimization of caustic concentration should be studied.

SUMMARY

A laboratory study of alkaline waterflooding, of two Saskatchewan heavy oils, has been conducted. The objectives of the study were to (i) assess the potential of the process for enhancing the recovery of these, and similar, heavy oils, and (ii) to investigate the controlling process mechanisms.

Interactions of various candidate alkaline injection fluids with oil, formation water, and reservoir core material have been examined under idealized laboratory conditions. The emphasis has been on assessing the relative effects of the alkaline additives, sodium hydroxide and sodium orthosilicate at various concentrations, in comparison with plain brine-flooding. The work included characterization of the oils and injection fluids, qualitative assessment of the injection fluids-formation water interactions, wettability investigation using the sessile drop method, interfacial tension study employing the spinning drop technique, comparative synthetic and preserved core displacement experiments, emulsion examination, and alkali consumption estimation.

Under the conditions of the experiments, sodium hydroxide and sodium orthosilicate exhibited similar effects on the wettability, interfacial tension, and synthetic core displacement results. Different alkali concentrations, on the other hand, had significantly different effects on the measured properties and displacement characteristics. Thus, a wettability reversal was observed, for example, at high sodium hydroxide concentrations (10 $\mu\text{g/L}$). While the alkalies have generally resulted in a significant IFT reduction, IFT showed a pronounced minimum trend with alkali concentration (more than two orders of magnitude IFT reduction at 0.1 g/L alkali concentration). The salinity of the alkaline fluid and the prevailing temperature were also found to have a definite effect on the measured interfacial tension.

Both synthetic and preserved core displacement studies showed the two Saskatchewan oils, from West Edam and one from Buffalo Coulee, to respond well to alkaline fluid injection. Thus, significant oil recovery improvements, up to 50% over brine injection, were observed in the laboratory. The alkali concentration effect, on oil recovery, was in good agreement with the IFT trends. The improvement appears to be due to the combined effect of a number of mechanisms. These include IFT reduction, favourable wettability changes, and emulsification. Statistical design of experiments and analysis of the synthetic core displacement results revealed a number of interesting effects. The analysis showed that the most significant effect was due to the type of oil (Buffalo Coulee oil responded better to alkali injection). Also significant were alkali concentration and injection rate, with the effects being comparable to each other. The alkali type, on the other hand, had an insignificant effect on the synthetic core recovery results.

The most important finding of the study is that the oil recovery improvement due to alkaline injection into the synthetic core system approaches that of steam in similar cores and laboratory set-ups. This finding suggests a good potential for the process with the examined, and similar, heavy oils. The rock reactivity study, however, indicates the potential for strong interactions between the alkalies and reservoir material. This suggests that further detailed chemical laboratory studies of these interactions are needed before the feasibility of pilot testing such a process can be fully defined. Moreover, because of the complexity of the various fluid-rock interactions, the process appears to be very strongly site-dependent. The use of reservoir materials in scaled experiments, under conditions approaching those in the field, is also recommended.

CONCLUSIONS AND RECOMMENDATIONS

Interactions of alkaline injection fluids with a number of Saskatchewan heavy oils, reservoir formation waters, and reservoir core material have been studied, under idealized laboratory conditions, from a variety of angles. The following main conclusions and recommendations have been derived from the study:

- . Formation of precipitates was confirmed when W. Edam formation water was contacted with either sodium hydroxide or sodium orthosilicate. Semi-quantitative elemental analysis suggested that these precipitates were calcium and magnesium silicates (in the case of sodium orthosilicate), calcium carbonate and/or magnesium hydroxide. The formation of these precipitates must be carefully assessed for any proposed pilot project. Such precipitates have the potential for permeability damage, on one hand, as well as the potential for beneficial flow diversion effects, on the other hand. Moreover, the precipitation of calcium and magnesium can increase alkali consumption, on one hand, and can result in IFT reduction, on the other. The effect of divalent ions on the IFT characteristics was not studied in this project; such a study is, therefore, recommended.
- . Wettability study of quartz/W. Edam heavy oils/alkaline injection fluid systems showed that sodium hydroxide and sodium orthosilicate have similar effects, at similar concentrations, on the contact angle of these systems.
- . The salinity and alkali concentration had a clearly observable effect on the contact angle and wettability characteristics of the systems. The smallest contact angles were observed in the case of distilled water. The contact angles remained largely unaffected by the elapse of time in the distilled water system. A tendency of the oil drops to spread on quartz with time (intermediate wettability or even oil-wet condition) was observed in the case of brine. With the exception of the case of 10 g/L NaOH in brine, water wet conditions prevailed in all quartz/W. Edam oil/alkaline solutions in brine systems.

In the case of 10 g/L NaOH solution in brine, complete immediate spreading of oil drops on the quartz plate was observed, indicating oil wet conditions.

- . For a specific pilot site, it is recommended that contact angle measurements be made using actual reservoir fluids.
- . As in the sessile drop study, sodium hydroxide and sodium orthosilicate had comparable effects, at the same concentrations, in reducing the interfacial tension of three Saskatchewan oils from W. Edam and Buffalo Coulee.
- . The Buffalo Coulee oil exhibited significantly lower IFT's than the two W. Edam oils, at equivalent conditions of alkali type and concentration.
- . The two W. Edam crudes exhibited a slight decrease in IFT with an increase in temperature from 20° to 30°C.
- . The spinning drop study showed that the IFT, of the two W. Edam oils, falls rapidly to a minimum in the presence of low concentration of alkali in brine (either sodium hydroxide or Metso 200 at 0.1 g/L brine). IFT, then, begins to increase with increased alkali concentration.
- . The presence of NaCl in the aqueous phase plays an important role in lowering IFT. In the absence of NaCl, a higher alkali concentration was required to reduce IFT to the same minimum levels. The optimum NaCl concentration in the injected alkaline fluid must be determined for each specific project.
- . Correlations have been developed for the IFT of W. Edam/alkali solution in brine systems. The correlations predict IFT, with good accuracy, as a function of alkali concentration, or pH, for each system.
- . Both sodium hydroxide and sodium orthosilicate had very favourable effects on oil recovery and water-oil ratios in synthetic core displacement experiments. The increase in oil recovery due to alkaline fluid injection, over distilled water or brine flooding, amounted to about 50% in some of the cases. A decrease in water-oil ratios of comparable magnitude was observed.

- . Analysis of variance of the factorially designed W. Edam oil displacement experiments showed that better recovery results are obtained at the 0.1 g alkali/L brine solutions, and at the higher feed rate. Moreover, while the effects of alkali concentration and feed rate were statistically significant, the effect of alkali type was not found to be significant. The displacement experiments findings were in good agreement with the IFT trends.
- . Significant improvement in oil recovery, due to alkaline fluid injection, was also obtained in the case of the Buffalo Coulee oil. In comparison with the W. Edam crude, the Buffalo Coulee oil showed somewhat higher oil recovery and lower water-oil ratios.
- . Unlike the W. Edam oil, analysis of variance of the set of Buffalo Coulee displacement experiments showed no statistically significant differences between feed rates, alkali types or concentrations. The generally high oil recoveries of the Buffalo Coulee oil appear to have masked these differences.
- . The difference between the recoveries of the W. Edam and Buffalo Coulee oils was verified by statistical analysis of the combined sets of displacement results. The effects of alkali concentration and injection rate followed the oil type in their statistical significance. Again, statistical analysis of the combined sets of results confirmed that there was no significant difference between the effect of sodium hydroxide and sodium orthosilicate.
- . The effects of salinity and divalent ions concentration in the connate water on the displacement results have not been studied in this project; they are worth investigating in future work. The effect of other alkaline additives, e.g. sodium carbonate or meta-silicate, may be also useful to examine in systematic core displacement studies. Sand cores with added known amounts and types of clays would also yield very valuable information on recovery efficiency and alkali/clay interactions.

- . Alkaline flooding at elevated temperatures, in conjunction with alkali consumption studies, is another area recommended for future research.
- . Improved oil recoveries due to alkali injection have also been confirmed in preserved core displacement experiments.
- . After a brine flood of a preserved core, nearly 0.3 HCPV of additional oil was recovered due to the injection of 0.1 g/L NaOH solution.
- . For a specific field application, a statistically designed program of preserved core displacements is recommended.
- . Formation of water-in-oil and oil-in-water emulsions was observed in standard alkali solution/crude oil emulsification tests. Emulsions were also observed in the produced fluids of core displacement experiments.
- . The oil recoveries, and oil recovery improvements, obtained as a result of alkaline fluid injection in synthetic sand cores, at room temperature, are comparable to those obtained with steam in similar laboratory systems. Notwithstanding the possible adverse impact of alkali interactions with real reservoir rocks, this finding indicates a good potential for the alkaline waterflooding process. The preserved cores oil recoveries, due to alkaline fluid injection, also approach those of steam laboratory displacements.
- . For certain minerals the alkalinity consumption can be significant, e.g. anhydrite and clays. Thus, the mineralogy of formations considered for alkaline floods would have to be a key area for study.
- . Since low concentrations of calcium and magnesium ions adversely affect IFT's and form precipitates with caustic flood chemicals, the cation exchange capacities of cores should be determined and the exchanged ions analyzed quantitatively.

- . Dynamic tests with alkali using cores in series are recommended to better define caustic consumption and identify potential reservoir damage problems. Effluents from these tests should be analyzed for metals and alkali as well as precipitates.
- . The effect of flow rate in dynamic tests on alkali consumption and precipitation should be determined so that optimum field injection rates can be estimated.
- . Static tests with various core/fluid ratios and reaction times would also be valuable in defining the types and rates of alkali consumption reactions.
- . A study of the effect of the reaction products from the above experiments on IFT's would also be valuable.

PART I - BACKGROUND

1. LITERATURE REVIEW

In conventional light oil reservoirs caustic flooding is used to mobilize residual oil after waterflooding to an economic limit. In heavy oil reservoirs primary production is normally very low; approximately 4% with a possible increase to 10% in recovery by conventional waterflooding [1]. To improve on these recoveries, caustic flooding is envisaged as a secondary recovery process.

Scott et al [2] found that recovery by caustic flooding of a 1200 cP (Lloydminster) crude increased by 4% and 31%, in comparison with a waterflood, for caustic concentrations of as little as 0.01 and 0.5% respectively. Farouq Ali et al [3], in a laboratory study, found an increase in the recovery of a Lloydminster crude from 32.1% for a waterflood to 60.3% when 2 PV's of caustic solution were injected. They also concluded that a caustic slug of at least 0.25 PV was needed for a significant recovery increase, and that continuous injection was more effective than slug injection. Dranchuk et al [1] reported recovery improvements similar to Farouq Ali for Lloydminster crude displacements by waterfloods containing concentrations greater than 0.1% NaOH.

Caustic flooding is believed to effect additional oil recovery by the following basic mechanisms [4]:

- (a) Reducing interfacial tension (IFT) between crude oil and water.
- (b) Modifying the wettability at the solid-liquid interface.
- (c) Emulsification and entrainment.
- (d) Emulsification and entrapment.
- (e) Solubilization of rigid interfacial films.

While IFT reduction and wettability reversals are the primary mechanisms involved in caustic flooding of light oils, it is thought that the mechanisms of emulsification and removal of interfacial films also contribute to improved recovery in high viscosity oil reservoirs.

Regardless of which of the mechanisms is involved in any one caustic flooding project, the success of caustic flooding relies on a chemical reaction between the caustic solution and the polar components present in the crude. Caustic reactions with organic acids, primarily carboxylic acids and to a lesser extent carboxyphenols, porphyrins or asphaltenes [5], lead to in situ generation of surfactants or sodium soaps. This results in the formation of emulsions, wettability reversals, and weakening of rigid or viscous interfacial films.

A most widely quoted measure of caustic reactivity with a certain oil is the acid number. An acid number of 0.2 mg KOH/g crude has been quoted by the National Petroleum Council as a minimum for considering alkaline flooding for light oils. Other values have also been proposed [4,6,7]. Acid numbers for crude oils can range from zero to 6.4 mg KOH/g. While various minimum acid numbers have been suggested, higher acid numbers do not necessarily result in higher oil recoveries. In fact, there appears to be no direct correlation between the acid number of an oil and the magnitude of enhanced recovery [5]. There seems to be a widespread agreement, now, that a better indicator of alkaline activity is a measurement of the interfacial tension. But, even the latter is probably strictly useful only as a screening tool [8].

Most alkaline floods have used sodium hydroxide or sodium orthosilicate with concentrations of up to 5 wt.%. Other alkaline additives, which have been tested in the laboratory or used in field applications, include sodium metasilicate, ammonia and sodium carbonate [5].

Campbell [9] compared the performance of sodium orthosilicate and sodium hydroxide for alkaline waterflooding. He found that in softened water, with no Ca^{++} or Mg^{++} ions present, both alkaline additives exhibit similar reductions in interfacial tension with all the crude samples tested. When unsoftened water was used to prepare alkaline injection solutions for mid-continent crudes, sodium orthosilicate outperformed sodium hydroxide in significantly reducing IFT values, even when NaOH was applied at much higher concentrations. For California crude oils, the effect of both additives, in reducing IFT, was comparable to each other

even when unsoftened solutions were used. However, a later study by Campbell [10], for a Wilmington California field, showed significant residual oil recovery from watered-out sand-packs when sodium orthosilicate was used at concentrations of 0.2 to 0.6%. Very low recovery yields were obtained, on the other hand, when sodium hydroxide was used at 0.2% concentration; no further tests were carried out at higher NaOH concentrations.

Jennings et al [11] concluded that caustic flooding at concentrations in the range of 0.05 to 0.5 wt.% NaOH resulted in in situ emulsification of heavy crudes and significantly improved oil recovery before breakthrough and lower WOR during the flood. IFT's between caustic and crude of substantially less than 0.01 mN/m (dyne/cm) were specified as being required for the success of the process.

It has been observed [1,7] that formation water composition can have an important effect on IFT and that the presence of sodium chloride reduces the amount of alkaline additive required for a specific reduction in IFT. Calcium and magnesium ions, on the other hand, increase the amount of caustic required. It was, thus, noted [7,9,11] that the presence of these ions in the reservoir water can inactivate the naturally occurring surface active acids, reducing the IFT lowering capability of the caustic. It was also noted [11] that certain multivalent ions can precipitate as insoluble hydroxides, carbonates or silicates with the addition of most alkaline additives to field water samples. If properly controlled and located, these precipitates can act as diverting agents to reduce the fingering and channeling and improve the sweep efficiency and oil recovery [5].

Reactivity of alkaline solutions with silica at moderate temperatures is relatively slow and incomplete. Detailed reaction rate studies, e.g. [12], have found that the reaction rate of the process is dependent on temperature, alkali concentration, alkali type, minerals present and available rock surface area. Reactions with certain clay components, in contrast with silica, may be significant. Clays with high ion exchange capacity can significantly enhance caustic consumption. Exchange of sodium, from an

alkali, for calcium and magnesium in the clays may result in the formation of precipitates, which may be accompanied with flow diversion, and/or clay swelling. Sodium/hydrogen ion exchange, on the other hand, is fast and reversible causing only a lag in the transport of the alkaline slug through the formation. Alkali/rock reactions may also have an influence on oil recovery through wettability changes of the mineral surfaces. It is generally believed [13] that such reactions result in altering the rock wettability from water-wet to oil-wet.

Wettability change was one of the first mechanisms to be suggested to explain the enhanced oil recovery associated with alkaline flooding [13]. Reservoir wettability depends on the extent of naturally occurring polar components present in the crude oil. Such components may be adsorbed onto the hydrophilic mineral surfaces rendering them hydrophobic. Sandstone wettability is particularly sensitive to high molecular weight hydrocarbons and asphaltene containing crude oils. Denekas et al [14] have clearly demonstrated the effect of high molecular weight hydrocarbons on wettability by individually examining the interactions of different distillation fractions, of numerous crude samples, with rock surfaces. They found the lower boiling point fractions to have little effect on wettability; but the influence increased with higher boiling point fractions to make the rock oil-wet. Improving oil recovery as a result of modifying the forces at the solid-liquid interfaces, i.e. by changing the preferential wettability, has been tested in a number of laboratory and field studies [15,16]. In these early studies, improved oil recovery was interpreted to be a result of reversing the rock wettability from oil-wet to water-wet. An alteration from oil-wet to water-wet, in a region where oil is continuous and flowing, changes the relative permeability of oil and water and provides a more favourable mobility ratio, improving oil recovery. Numerous investigations have been published in support of this mechanism, e.g. [8,17,18]. A distinctly different wettability reversal mechanism is that suggested by Cooke et al [7]. They proposed that caustic flooding can improve oil recovery by reversing the wettability of an originally water-wet rock to become oil-wet. In this mechanism, an originally discontinuous non-wetting residual oil is converted to a

continuous wetting phase which provides a flow path for what otherwise would be trapped oil. Based on similar observations, Ehrlich et al [6] point out that oil recovery improvement, obtainable from wettability alteration, depends on the amount of continuous oil present at the time the wetting change takes place.

The criterion for wettability as derived by Younge and Dupre is

$$\gamma_{ow} \cos \theta = \gamma_{os} - \gamma_{ws}$$

where γ_{ow} = IFT between oil and water.
 γ_{os} = IFT between oil and solid.
 γ_{ws} = IFT between water and solid.

θ = contact angle measured through water phase.

The equation indicates that lowering the oil-water IFT by caustic injection will result in the surface becoming more water wet (i.e. θ decreasing for $\theta < 90^\circ$). However, for intermediate or oil-wet surfaces (where $\theta > 90^\circ$) wettability reversal requires a change in the relative affinity of the solid for each of the two fluid phases, which is reflected by the difference in IFT between oil and solid and water and solid.

Wettability reversals, reduced capillary forces, and changes in relative permeability may not be the only major contributing factors to improved recovery in heavy oil-alkaline systems. This is unlike alkaline flooding of a light oil reservoir where wettability change is postulated to be the dominant EOR mechanism [6]. Important mechanisms and benefits of caustic injection in heavy oil reservoirs include in situ emulsification (generation, entrainment and entrapment), breaking of rigid interfacial films and consequent rheological and flow stability phenomena.

The lower API gravity viscous crude oils have generally a higher content and wider variety of natural petroleum acids, such that the naturally occurring emulsifiers (acids converted to soaps) in a single crude may range into the hundreds. Emulsification is believed to improve oil recovery by two mechanisms: entrainment and entrapment.

In the entrainment mechanism, small oil droplets are formed by emulsification, become dispersed, and are subsequently entrained in the alkaline drive water to be produced in high proportions at the producing wells [19]. The produced emulsions will, in general, lower the mobility of the displacing aqueous phase. This results in a more efficient displacement due to the improved mobility ratio.

In the entrapment mechanism, it is postulated [11,13] that residual oil, in a preferentially water-wet core, could be emulsified and moved downstream with the drive water only to be trapped again by smaller pore throats. The entrapment mechanism results in a reduced water mobility which improves vertical and areal sweep efficiency. This flow diversion mechanism is especially important in the waterflooding of viscous oils, where the sweep efficiency is known to be very poor [13,19].

It is known that rigid or viscous films of asphaltic and resinous materials form at the crude oil-water interfaces (particularly heavy oil-water interfaces), e.g. [5,6]. The rigidity of these films is reduced when the water is made alkaline [20,21]. Improvement in oil recovery may, therefore, be achievable due to the decreased flow resistance resulting from the solubilization of films which block pore constrictions. This improvement may be especially significant in highly heterogeneous porous media. The presence of film material has also an important effect on the stability of emulsions; as the films tend to form physical barriers which inhibit contact between the dispersed droplets. The pH of oil-brine emulsions was identified [21,22] as the most important factor affecting the stability or breakability of these emulsions.

To summarize this background section, it is appropriate to highlight the current theory and views on the mechanisms of alkaline flooding. The summary given in the following is based on the preceding discussion of the literature as well as the major reviews of the subject which appeared over the last several years [4,5,13].

- . Alkaline chemicals, added to injection water, react with naturally occurring acids in crude oils (particularly high gravity oils) to produce surfactants in situ.
- . These surfactants can result in dramatic reduction in oil-water interfacial tension (down to IFT's in the range of 10^{-3} mN/m). Such low IFT's are believed to be directly responsible for mobilizing trapped and residual oil ganglia (this may be easily demonstrated by consideration of typical pressure gradients and capillary pressures).
- . The chemical reactions and low interfacial tensions are also believed responsible for the formation of emulsions (water-in-oil and oil-in-water). Emulsification leads to entrainment of very fine oil droplets with the alkaline solution (Emulsification and Entrainment). Emulsion droplets may also become only temporarily mobile, but get retrapped in down stream pore throats (Emulsification and Entrapment). This can improve the sweep efficiency by directing the injection fluid towards undisplaced flow channels.
- . Changes in wettability may take place due to the adsorption of soap molecules (formed by interfacial reactions) on the reservoir rock. A reversal from oil-wet to water-wet condition can result in favourable mobility changes in the regions where oil is flowing. A reversal from water-wet to oil-wet can provide flow paths for discontinuous residual oil. Within a reservoir, wettability is not generally a discrete-valued function, but spans a continuum between the two extreme conditions (oil-wet and water-wet). Oil recovery improvement from wettability reversals, thus, depends on a number of factors such as the amount of continuous oil present during wettability alteration, fractional flow of oil and water, and oil-water viscosity ratio. Wettability reversal, therefore,

depends on the alkaline water-oil interactions, fluid-solid interactions, reservoir characteristics and conditions, and the alkaline water injection schemes.

- . Some crude oils form insoluble rigid films at the oil-water interfaces. These films can have an unfavourable effect on oil displacement in heterogeneous porous media. There are suggestions that alkaline additives may play a role in the solubilization of these films, to improve oil recovery.

PART II - STUDY PROGRAM

2. FLUIDS CHARACTERIZATION

The fluids considered at various stages of this project included Saskatchewan heavy crude oils, associated formation waters, synthetic brine solution, and prepared alkaline injection fluids.

Two well-head crude oil samples, and their associated formation water, were obtained from Gulf West Edam wells. A third well-head oil sample, with no formation water, was obtained at a later stage of this project from Saskoil. No field additives were present in any of the samples. The respective wells sampled are:

- . Gulf West Edam Well 5-30-48-20W3 drilled in the Sparky formation.
- . Gulf West Edam Well 12-6-49-20W3 drilled in the Waseca formation.
- . Saskoil Buffalo Coulee Well D7-22-32-24W1.

Two alkaline additives (sodium hydroxide and sodium orthosilicate) were used in the study. Only crystalline sodium orthosilicate known commercially as METSO 200 was employed throughout this work. The manufacturer's specifications of this material are listed in Table 1. Solutions of the two alkaline additives in brine were prepared at concentration levels in the range of 0.1 to 40 g/L.

2.1 Crude Oil Analysis

Several standard ASTM and Gulf analytical procedures have been conducted to determine the basic chemical and physical characteristics of the three heavy crude oils. Tables 2-4 list the analytical results for the original (as received) as well as dried samples of each of the three crudes. Only dried oil was used throughout the various phases of this project. This was necessary to maintain uniformity and consistency of results, and to be able to set meaningful comparisons. Drying was carried out either by centrifugation or by distilling off the water and recombining the oil light and heavy ends. Both methods yielded oil with GCD characteristics very similar to the original sample, as exemplified in Figure 1.

TABLE 1

MANUFACTURER'S SPECIFICATION FOR SODIUM ORTHOSILICATE
METSO 200*

Mol. Ratio $\text{Na}_2\text{O}:\text{SiO}_2$	2:1
% Na_2O	60.8
% SiO_2	28.8
% H_2O	9.5
Approximate sizing	10 mesh - 65 mesh
Approximate density kg/m^3	untamped 1009 tamped 1201
Description	crystalline anhyd. sodium orthosilicate

* (Obtained from National Silicates Ltd. - an affiliate of
the PQ Corp. - Toronto, Ont. M8V 3S7)

TABLE 2

CRUDE OILS CHARACTERISTICS

	<u>Method*</u>	<u>Well #5-30-48-20-W3</u>	
		<u>Original</u>	<u>Dry</u>
Specific Gravity, °API	Calculated	13.2	13.9
Density (g/mL) 15°C	D4052-81	0.9771	0.9724
65°C	D4052-81	0.9462	0.9387
Viscosity (cSt) 25°C	D445	2585	3411
40°C	D445	646.9	714.5
Water Content, %	D95	2.6	0.0
Total Acid Number			
(mg KOH/g oil)	D664	0.96	--
Salt Content, ppm	GCM 117	1520	--
Ramsbottom Carbon			
Residue, R.C.R. %	D524	10.3	--
Bottoms Sediment & Water	D96	4.2	--
Pour Point, °C	D97	-15.0	-6.0
Sulphur, %	D2622	4.12	4.10
Mercaptans/			
H ₂ S, ppm	GCM 118	1660/NIL	--
Total Nitrogen, ppm	D3228	2887	--

*NOTE: D - ASTM Method
GCM - Gulf Canada Method

TABLE 3

CRUDE OILS CHARACTERISTICS

	<u>Method*</u>	<u>Well #12-6-49-20-W3</u>	
		<u>Original</u>	<u>Dry</u>
Specific Gravity, °API	Calculated	11.0	12.5
Density (g/mL) 15°C	D4052-81	0.9926	0.9822
65°C	D4052-81	0.9620	0.9495
Viscosity (cSt) 25°C	D445	6508	8954
40°C	D445	1847	1911
Water Content, %	D95	12.5	0.0
Total Acid Number			
(mg KOH/g oil)	D664	1.00	--
Salt Content, ppm	GCM 117	3116	--
Ramsbottom Carbon			
Residue, R.C.R. %	D524	9.6	--
Bottoms Sediment & Water	D96	16.0	--
Pour Point, °C	D97	-4.0	-3.0
Sulphur, %	D2622	3.97	3.97
Mercaptans/			
H ₂ S, ppm	GCM 118	4160/NIL	--
Total Nitrogen, ppm	D3228	2799	--

*NOTE: D - ASTM Method
GCM - Gulf Canada Method

TABLE 4

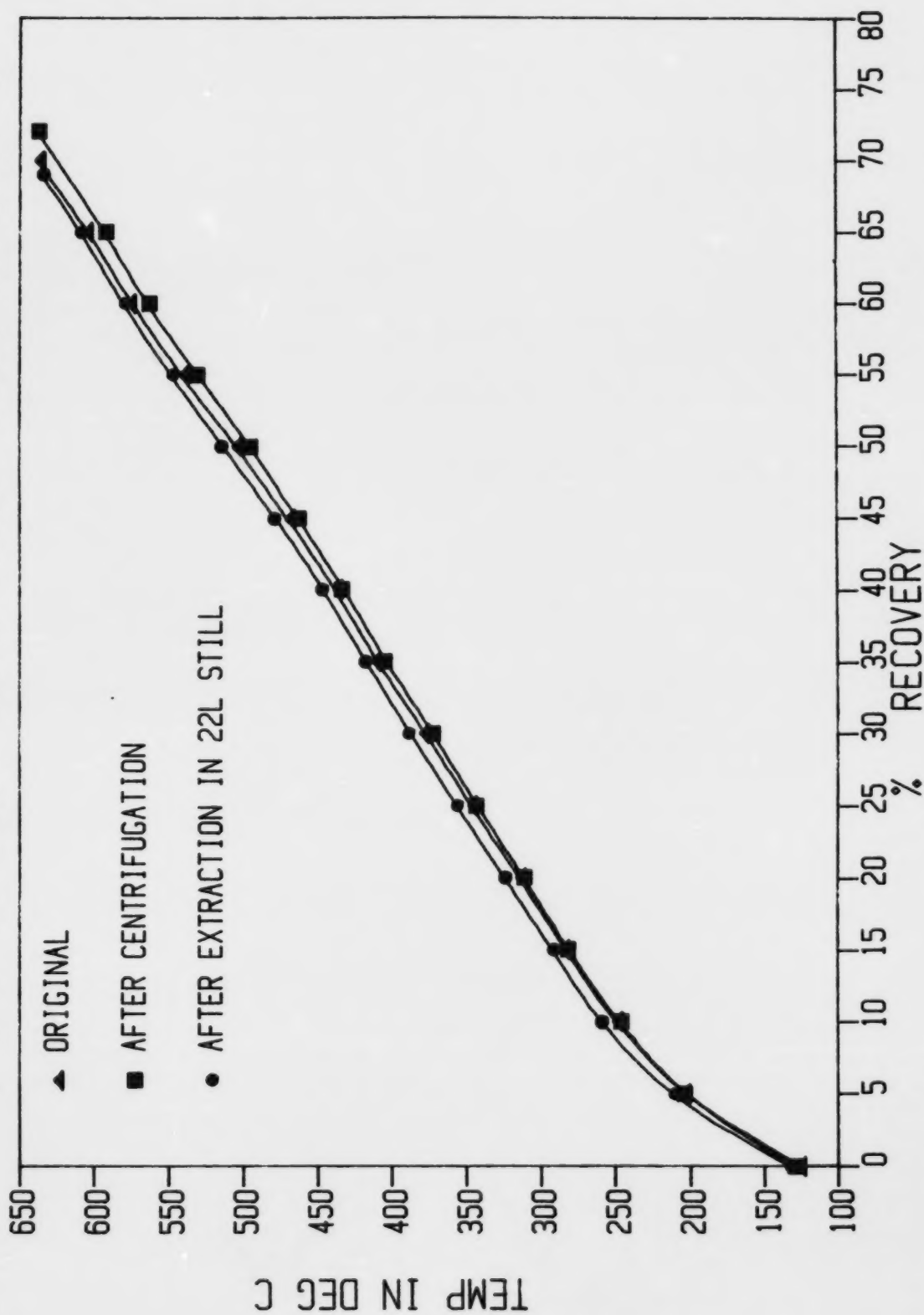
CRUDE OILS CHARACTERISTICS

	<u>Method*</u>	<u>Well #D7-22-32-24 W1</u>	
		<u>Original</u>	<u>Dry</u>
Specific Gravity, °API	Calculated	11.9	12.8
Density (g/mL) 15°C	D4052-81	0.9860	0.9801
65°C	D4052-81	0.9552	0.9492
Viscosity (cSt) 25°C	D445	6768.3	2858.6
40°C	D445	1914.9	886.1
Water Content, %	D95	29.4	0.1
Total Acid Number (mg KOH/g oil)	D664	0.85	0.80
Salt Content, ppm	GCM 117	1829	5454
Ramsbottom Carbon Residue, R.C.R. %	D524	2.47	--
Bottoms Sediment & Water	D96	0.5	--
Pour Point, °C	D97	-4.0	-3.0
Sulphur, %	D2622	1.17	3.43
Mercaptans/ H ₂ S, ppm	GCM 118	1126/NIL	1570/NIL
Total Nitrogen, ppm	D3228	2189	3363

*NOTE: D - ASTM Method
GCM - Gulf Canada Method

FIGURE 1

G C D OF WEST EDAM CRUDE 5-30-48-20-W-3



As can be observed from the tables, the characteristics of the three crudes are typical of Saskatchewan heavy oil reservoirs. An interesting feature of the Saskoil heavy crude is that, unlike the West Edam oils, the viscosity of the wet sample is more than double that of the dry sample. The high water content (29.4%) of the original sample appears to result in a high degree of emulsification (water-in-oil emulsion), which manifests itself by high viscosity of the wet sample.

It may be noticed from the tables also that the three oils have similar acid numbers (in the range of 1 mg KOH/g oil). It was originally believed by Saskoil that the Buffalo Coulee crude had an acid number in the neighbourhood of 2 mg KOH/g oil. This claim could not be substantiated by our own lab measurements. It will be shown, nevertheless, that, in spite of the similarity in acid number, the IFT response of the Buffalo Coulee oil to alkaline additives was noticeably different in magnitude from the West Edam oils.

2.2 Formation Water Compositional Analysis

Standard compositional analysis was carried out on the formation water samples corresponding to the two West Edam oils. No formation water sample was supplied by Saskoil with the Buffalo Coulee crude. Table 5 shows the ions detected in each of the two West Edam formation water samples, as well as the total dissolved solids in each.

For purposes of the IFT study and the comparative core-flooding experiments of this project, synthetic injection fluids were prepared to contain only sodium chloride. No attempt was made to include other ions (e.g. Ca, Mg, SO₄ ...) which, even in the actual formation water, are present only at relatively low concentrations (see Table 5). The concentration of sodium chloride was selected to match the level which is usually observed to yield high interfacial activity in similar systems [23]. The selected brine solution, used throughout this work, contained 5.084 g/L NaCl. This solution was also used as the base for all the alkaline injection fluids of the study.

TABLE 5

ANALYSIS OF WEST EDAM FORMATION WATER SAMPLES

	<u>Sample</u> <u>5-30-48-20-W3</u>		<u>Sample</u> <u>12-6-49-20-W3</u>	
Relative Density, 15°C	1.0476		1.046	
pH	7.6		8.5	
<u>Ion</u>	<u>Conc</u> <u>g/m³</u>	<u>Conc</u> <u>mol/m³</u>	<u>Conc</u> <u>g/m³</u>	<u>Conc</u> <u>mol/m³</u>
Na	20599	896	20875	908
K	427	10.9	430	11.0
Ca	680	17.0	705	17.6
Mg	730	30.0	700	28.8
Fe	0.7	0.013	1.8	0.032
Cl	37800	1066	37600	1060
HCO ₃	673	11.0	2173	35.6
SO ₄	28	0.291	28	0.291
CO ₃	0.0	0.0	15.6	0.260
H ₂ S	--	--	--	--
Si as SiO ₂ , ppm	7.5		10.1	
Total Dissolved Solids g/m ³ "calculated"	60700		61300	

2.3 Properties of Alkaline Injection Fluids

Solutions of sodium hydroxide as well as solutions of sodium orthosilicate in brine (5.084 g/L NaCl) were prepared as candidate injection fluids. The concentration of alkaline additive ranged from 0.1 to 40 g/L brine. The properties of the prepared solutions, relevant to this study, have been measured and are reported in Table 6.

2.4 Compatibility of Alkaline Injection Fluids with Formation Water

Compatibility of the candidate alkaline injection fluids with the West Edam formation water samples was tested to identify potential benefits or otherwise reservoir damage problems.

Sodium hydroxide (0.1 N) was mixed, in equal volumes, with each of the W. Edam formation waters. Similarly, sodium orthosilicate solutions (4 g/L) were mixed with the formation water samples. In all four cases, formation of precipitates was observed. This was considered an indication of formation of the highly insoluble calcium silicates, calcium carbonate and/or magnesium hydroxide. To verify this, the precipitates obtained with the sodium orthosilicate solutions and the two formation water samples were filtered and analyzed. Table 7 shows the results of a semi-quantitative elemental analysis of the precipitates. The high content of Ca, Mg and Si confirms the formation of the abovementioned insoluble salts.

There are suggestions in the literature [5] that, if properly located, these precipitates can cause diversion of flow within the reservoir, leading to better contact of the injected fluid with the less permeable flow channels. This is a possible contributing factor to improved oil recovery. Furthermore, the reduction in reservoir brine cation activity may lead to lower IFT values. This appears to be the reason for the more favourable results sometimes obtained with sodium orthosilicate over sodium hydroxide (calcium and magnesium silicates are much less soluble than the corresponding hydroxides). On the other hand, it is also conceivable that precipitates such as calcium silicate can cause adverse plugging of the reservoir.

TABLE 6

PROPERTIES OF CANDIDATE INJECTION FLUIDS

	Conc g/L	pH	Density g/mL		Viscosity cSt	
			15°C	65°C	25°C	40°C
Sodium Orthosilicate in Brine	0.1	10.61	1.0028	0.9720	0.93	0.68
	0.4	11.50	1.003	0.9725	0.92	0.68
	1.0	11.90	1.0037	0.9729	0.95	0.70
	4.0	12.47	1.0070	0.9761	0.95	0.69
	10.0	12.83	1.0133	0.9822	0.96	0.70
	40.0	13.28	1.0442	1.0121	1.07	0.79
NaOH in Brine	0.1	11.01	1.0028	0.9720	0.93	0.67
	0.4	11.74	1.0031	0.9723	0.93	0.68
	1.0	12.14	1.0038	0.9730	0.95	0.69
	4.0	12.75	1.0071	0.9762	0.94	0.69
	10.0	13.07	1.0135	0.9825	0.95	0.68
	40.0	13.50	1.0444	1.0120	1.08	0.79
Brine Solution		6.2	1.0026	0.9718	0.92	0.68

TABLE 7

SEMI-QUANTITATIVE ELEMENTAL ANALYSIS OF
SODIUM ORTHOSILICATE/FORMATION
WATER PRECIPITATES

	Well #5-30-48 wt.%	Well #12-6-48 wt.%
Al	<<0.1	<<0.1
Ca	>10	>10
Cu	<0.1	<0.1
Fe	--	≈0.1
Pb	<0.1	<0.1
Mg	>10	>10
Mn	<0.1	<0.1
Si	>10	≈10
Ag	<<1	<<1
Na	>5	>5

3. WETTABILITY INVESTIGATION

It is well established that the wettability characteristics of oil-water-rock systems play a major role in oil recovery. It has already been pointed out that many alkaline additives are believed to be capable of initiating a wettability reversal mechanism, which could have significant influence on enhancing heavy oil recovery. Therefore, knowledge of the preferential wetting tendencies of a particular system, under various conditions, gives a valuable insight into controlling a major oil recovery enhancement factor.

The contact angle provides the only direct measurement of the wettability of a given oil-water-rock system. Imbibition or drainage-type experiments are frequently employed [17,24]; but give only an indirect-determination of the wettability characteristics of a system.

In principle a contact angle measurement is simple; a drop of oil is placed on a mineral surface in the presence of formation water, and the angle through the water phase is measured. If the angle is small ($<40-75^\circ$), the surface is water-wet. If the angle is large ($>105-140^\circ$), the surface is oil-wet. In between these arbitrary limits, an intermediate wettability condition is said to exist. In practice, however, the observed contact angle is sensitive to many factors such as the manner in which the three phases are brought into contact, time allowed for the interfaces to reach equilibrium, and any trace contaminants present. The usefulness of a contact angle measurement also depends on how closely the reservoir conditions are simulated. Over the last twenty years, nevertheless, a large body of contact angle data has become available [25].

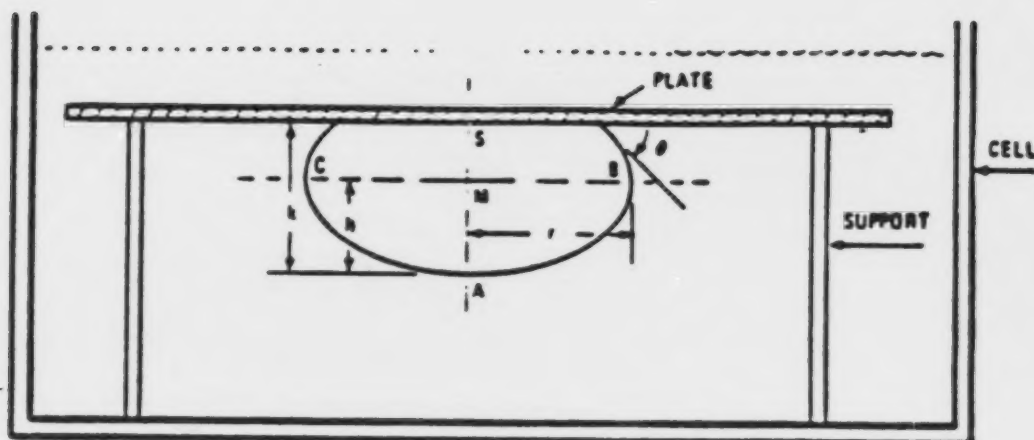
It was important, for the above-mentioned reasons, to investigate the wettability characteristics of the solid/oil/injection fluid systems under consideration. This was carried out by visual observation of oil drops formed on a quartz surface in the presence of alkaline solutions, brine or distilled water. For this visual study, the sessile drop technique, as described in the API RP42 procedure, was used.

3.1 Sessile Drop Method

The sessile drop method involves injecting a small drop of oil on the underside of a flat polished mineral surface in a cell filled with water or other injection fluid, Figure 2. The maximal dimensions of the drop can be used to calculate the system's interfacial tension and contact angle. The contact angle can, alternatively, be determined through a direct measurement on an enlarged photograph, as illustrated in Figure 2. The sessile drop technique became particularly popular after the significant computational developments made by Staicopolus [26-28] and Brandner and Melrose [29] during the early and mid 1960's. They presented detailed calculations of meridional sections of a sessile drop in the form of tables containing accurate values of the coordinates of points on the surface of the drop, surface area, volume, and the centre of gravity of sections across the drop. Shape correction factor tables and graphs were also developed to facilitate utilizing the method.

Although the sessile drop technique is simple in principle, numerous experimental difficulties are known to be associated with the method [30], particularly for low IFT systems. In the recent thorough investigation by Reed and Healy [30], they found that the precision of the contact angle measurement decreases with the decrease of IFT of the system. Moreover, when the IFT is very low (of the order of 10^{-3} mN/m), they pointed out that it may not be possible to form a drop; instead, fluid can stream out of the needle and disperse completely. Also, only a small range of droplet shapes can be conveniently considered using this method. Flat drops have usually obscure profiles near the three phase contact, such that a direct contact angle measurement becomes very inaccurate. More rounded drops, on the other hand, do not allow using the API RP42 calculation procedures and correlations. Roughness of substrate surface, contamination of fluids and surfaces, and time allowed for equilibration are other major concerns. Treiber et al [25], for example, pointed out that water-wet systems under anaerobic conditions could show oil-wet results after being aerated. Trace metal ions (as low as 10 ppm copper and nickel ions) were reported to reverse the wettability of a number of systems from water-wet to oil-wet.

FIGURE 2
SESSILE DROP CONFIGURATION
AND CELL DESIGN



It was also emphasized that treating, stimulation or corrosion inhibiting materials should not be present when sampling an oil well for wettability testing.

3.2 Experimental Procedure

As mentioned earlier, the API RP42 procedure for wettability evaluation was followed for the contact angle study using the sessile drop technique. Several glass, and plexy glass, cells have been used in the study. Highly polished quartz plates were used as the solid substrate, to simulate the reservoir rock, throughout the work. The quartz plate was supported by small teflon prisms inside the cell.

The following steps were followed in each of the experiments:

- . The cell, teflon supports and quartz plate were thoroughly cleaned with solvent, rinsed with distilled water, and soaked in chromic acid for several hours. The chromic acid was then removed by repeated rinsing with distilled water. Final washing of all the components was made using a large de-gased quantity of the injection fluid being considered.
- . The cell, with the quartz plate and supports, was then filled with the injection fluid (brine, distilled water, or alkaline solution of sodium hydroxide or sodium ortho-silicate in brine).
- . The solution was permitted to age in the cell for at least 24 hours.
- . Using a hypodermic syringe, a droplet of oil was placed on the underside of the quartz plate.
- . The change in drop shape and dimensions, with time, was visually observed and recorded with a microscope/camera arrangement.

In all the experiments it was ensured that the system reached equilibrium, i.e. the drop dimensions reached constant values. Several hundred hours were sometimes required to reach the

equilibrium dimensions. It was further ensured that the drop was symmetrical, i.e. had the same shape when viewed from any direction parallel to the plate on which the drop rested. Violation of the latter condition indicates a non-uniformity in the plate smoothness or contamination of the surface. When this condition was encountered, the remedy was to change and/or clean the plate before refilling the cell with the aqueous phase.

In this contact angle study only one West Edam oil (5-30-48) was considered. The injection fluids were distilled water, brine, sodium hydroxide solutions in brine, and sodium orthosilicate (Metso 200) solutions in brine. Concentrations of 0.1, 1.0 and 10.0 g/L of each alkali in brine were examined in combination with West Edam (5-30-48) oil. Only quartz plates were employed as the solid substrate to represent the wettability characteristics of the reservoir sand.

3.3 Sessile Drops Results and Observations

Figures 3 to 10 show the results of the wettability study in the form of several series of sessile drop photographs. Each figure shows the variation of a sessile drop shape and dimensions with time, for a specific additive solution, brine or distilled water. Figure 11 summarizes some of these results by comparing the effect of sodium hydroxide with sodium orthosilicate after 5 days of oil drop injection in each case. The ratio of the sessile drop photograph dimensions to actual drop dimensions is 14:1 in each case.

Within the constraints of the large errors associated with the sessile drop technique (Sec. 3.1), Table 8 provides the estimated contact angle and h/r ratio (height of drop from apex to equatorial plane h to the equatorial plane radius r). The estimates are based on direct measurements using the sessile drop photographs, after the drop reaches its equilibrium shape. In each case the average of several measurements is reported. A number of interesting trends clearly emerge from the figures and Table 8, and are discussed in the following.

FIGURE 3

EFFECT OF TIME ON SESSILE DROP
IN 0.1 G/L METSO 200



4 DAYS, 6 HOURS



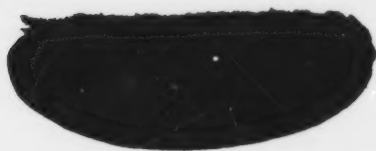
6 DAYS



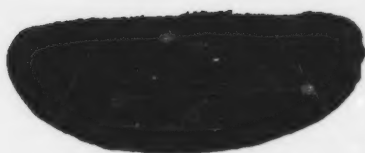
7 DAYS

FIGURE 4

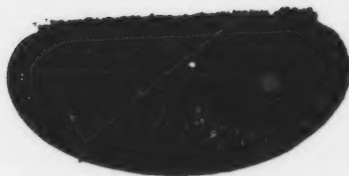
EFFECT OF TIME ON SESSILE DROP
IN 1.0 G/L METSO 200



1 DAY



2 DAYS



5 DAYS

FIGURE 5

EFFECT OF TIME ON SESSILE DROP
IN 10.0 G/L METSO 200



3 DAYS, 2 HOURS



2 DAYS, 19 HOURS



3 DAYS, 19 HOURS



4 DAYS



4 DAYS, 19 HOURS

FIGURE 6
EFFECT OF TIME ON SESSILE DROP
IN 0.1 G/L NaOH



17 HOURS



3 DAYS, 17 HOURS



4 DAYS

FIGURE 7

EFFECT OF TIME ON SESSILE DROP
IN 1.0 G/L NAOH



1 DAY



18 HOURS



4 DAYS



3 DAYS, 17 HOURS

- 40 -

FIGURE 8
EFFECT OF TIME ON SESSILE DROP
IN 10.0 G/L NaOH



FIGURE 9

EFFECT OF TIME ON SESSILE DROP
IN BRINE



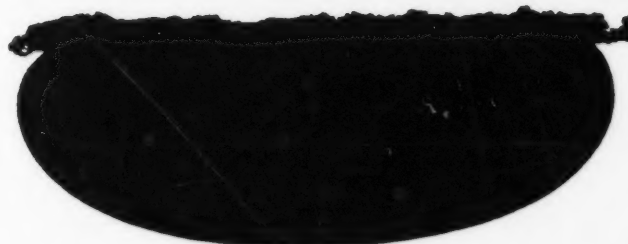
2 HOURS



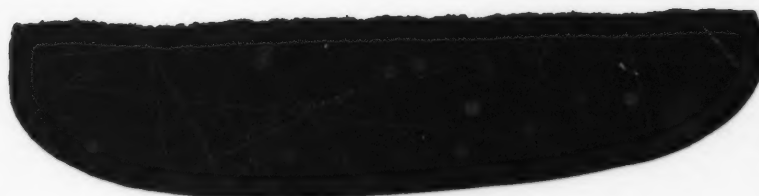
1 DAY



3 DAYS



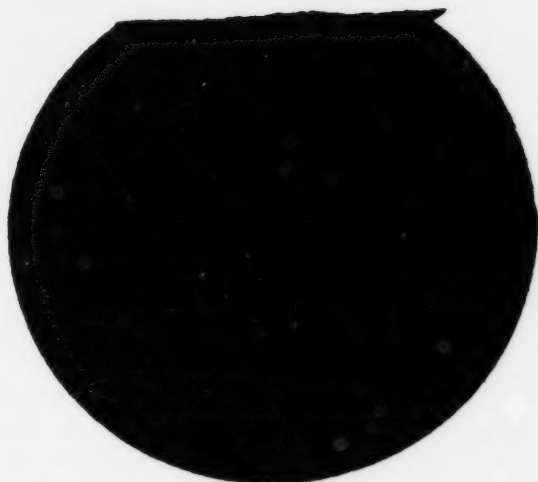
6 DAYS



8 DAYS, 17 HOURS

FIGURE 10

EFFECT OF TIME ON SESSILE DROP
IN DISTILLED WATER



2 HOURS



1 DAY



3 DAYS



6 DAYS



8 DAYS, 17 HOURS

FIGURE 11
Effect of Alkali Concentration on
W. Edam Oil Sessile Drops

SODIUM ORTHOSILICATE



0.1 g Na_4SiO_4 /L Brine

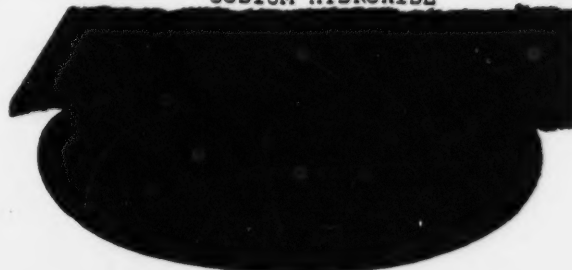


1.0 g Na_4SiO_4 /L Brine

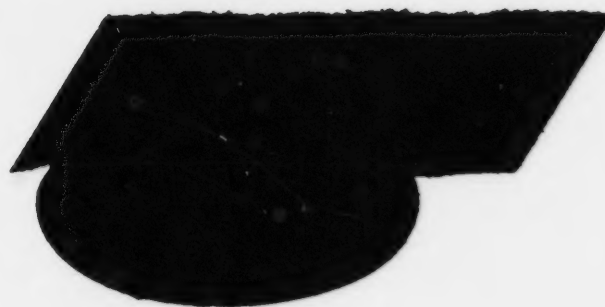


10 g Na_4SiO_4 /L Brine

SODIUM HYDROXIDE



0.1 g NaOH /L Brine



1.0 g NaOH /L Brine



10.0 g NaOH /L Brine

TABLE 8

WEST EDAM OIL SESSILE DROPS CHARACTERISTICS

<u>Water Phase</u>	<u>Contact Angle</u>	<u>h/r</u>
0.1 g/L NaOH in brine	34	0.44
1.0 g/L NaOH in brine	59	0.54
10.0 g/L NaOH in brine	--	--
0.1 g/L METSO 200 in brine	59	0.45
1.0 g/L METSO 200 in brine	40	0.57
10.0 g/L METSO 200 in brine	65	0.69
Brine	70 (increasing)	--
Distilled Water	23	0.90

With only two exceptions, a small acute contact angle, between the oil drop and quartz plate, was observed. This indicates that the systems examined, with two exceptions, were water-wet. As may be observed in Figures 8 and 11, the 10 g/L NaOH in brine solution resulted in immediate spreading of the oil drop on the quartz plate, indicating an oil-wet system. The experiment was repeated several times and the same observation was confirmed. The brine solution was the other exception where, in contrast with the 10 g/L NaOH, slow and gradual spreading of the oil drop took place. In this case the spreading manifested itself by a continuous decrease of the drop (h/r) ratio, until the drop became very flat.

The smallest contact angles were observed in the case of the distilled water system, Figure 10. The angle in this case remained largely unaltered for the duration of the experiment. This observation is in qualitative agreement with previous studies of similar systems [25]. In particular, it was found in the referenced study that pure hydrocarbons such as pure grade decane, when tested against quartz in conductivity water, gave nearly zero contact angle. The angle, moreover, was reported to remain zero, at room temperature, over a period of 1960 hours.

While the interaction of the oil-quartz system with distilled water is interesting, the contact angle behaviour in the presence of brine is more significant. The slow but continuous spreading of oil drops, in the latter case, indicates a tendency of the system towards intermediate wettability, or even oil-wet, conditions. This system represents a closer approximation of the field crude oil-formation water-reservoir rock conditions.

The addition of sodium hydroxide or sodium orthosilicate, as clearly observable in the photographs, results in a reversal of the wettability conditions which prevailed in the case of brine alone. Thus, strongly water-wet conditions appear to emerge with the addition of alkalies, particularly at the lower additive concentrations. All the above findings are in good qualitative agreement with previous wettability studies, e.g. [15,16,25]. In the referenced studies, it was found that mineral surfaces, on which contact angles were measured,

are strongly water-wet in the presence of surfactant free oil and water (compare with the present distilled water system observations). However, with some of the systems studied, high contact angles were measured after the oil had contacted the solid surfaces for a long time (compare with the age effect of the brine system). It was noted that these systems involved crudes containing natural surface-active materials capable of imparting oil-wetness to otherwise water-wet surfaces.

In the case of high sodium hydroxide concentration (10 g/L), another reversal to oil-wet conditions takes place. Cooke et al [7] were the first to identify that under certain conditions of salinity, pH and temperature, a change of wettability to preferentially oil-wet conditions could take place. The observed effect of sodium hydroxide concentration suggests that, for the present system and similar systems, a variable alkaline concentration may be desirable for optimum application. At the beginning of an alkaline flooding project, where oil saturation is high, a low caustic concentration would be beneficial. Conversely, when the oil saturation is low, a high caustic concentration would be more effective. The reason is that strongly water-wet conditions are favoured when the oil saturation is high (flowing oil conditions) to take advantage of the favourable mobility changes. Oil-wet conditions (associated with high caustic concentration), on the other hand, can provide flow paths for discontinuous residual oil at the low saturation levels. In practice, for a specific application, numerous factors would dictate the alkali concentration levels to be used at the various stages of the recovery process. As mentioned earlier, and will be further discussed later, these factors include, in addition to the nature of the oil in question and type of additive, such effects as salinity of the injected fluid, reactivity of injection fluid with the reservoir rock and the prevailing reservoir temperature.

Examining the sessile drop figures and table shows that the characteristic h/r ratio increases with increased additive concentration in brine. Noting that the density of all the tested solutions are fairly close, Table 6, the increase in h/r ratio indicates a corresponding increase in interfacial

tension. As will be shown in the next section, the spinning drop IFT measurements confirmed this observation. Also, in agreement with the spinning drop IFT measurements, very high h/r ratios (near 1) were observed for oil drops in distilled water and initially in brine. The spinning drop measurements indicated that the IFT of the distilled water and brine systems were two orders of magnitude higher than the oil-additive solution systems. The continued decrease of the oil drop h/r ratio, in the case of brine is due to the tendency of the drop towards oil-wetting conditions. This tendency results in the observed slow, but continuous, spreading of the drop over the quartz plate, as discussed earlier. Finally in the figures, it is clear that the h/r ratio trends are similar for the corresponding sodium hydroxide and sodium orthosilicate solutions.

With the exception of the 10 g/L NaOH solution in brine, the contact angle did not seem to have a definite trend with additive concentration. In the range of concentrations examined, and for the particular salinity of solutions, there is generally a slight tendency of contact angle to increase with alkali concentration. In all the cases, excluding the 10 g/L NaOH, the measured angle is less than 70. Again the contact angle trends are similar for corresponding NaOH and Na_4SiO_4 systems.

4. INTERFACIAL TENSION STUDY

The majority of studies in the open literature indicate that lowering of the oil-water interfacial tension is probably the dominant mechanism of enhancing oil recovery by alkaline flooding. It was, therefore, important to carefully analyze the IFT characteristics of the heavy crude-alkaline solution systems involved in this study. Only a few methods are suitable for measuring the low interfacial tension of such systems; and the spinning drop technique is known to be the simplest and most effective of these methods. It has been exclusively employed in this project for the IFT study of all heavy crude-aqueous solution systems.

In the following subsections a brief introduction to the spinning drop IFT measurement technique is given. A review of the relevant literature is also included. This is followed by the experimental details of our measurements, and discussion of the results obtained for three Saskatchewan oils.

4.1 The Spinning Drop Method

The method of obtaining interfacial and surface tension by measuring the shape of a liquid drop or a gas bubble in a more dense liquid contained in a rotating horizontal tube apparently had its origin in the experiments of Plateau [31] over a century ago. The method in its present form, however, was proposed by Vonnegut [32], who described the technique and reported some preliminary IFT measurements for gas-liquid systems. While some improvements to Vonnegut's method were reported, e.g. Rosenthal [33], a more complete theory for the technique was given by Princen et al [34]. It was not until the work of Cayias et al [35], and the refinements of Slattery and Chen [36], that the full utility of the method was realized. The theory of Cayias et al [35] is based on measuring both the length and width of the drop, rather than just one or the other as proposed in earlier developments. It had also the advantage of not having to measure the volume of the drop. Furthermore, the authors clearly demonstrated that the method is simple, accurate, and compares quite favourably with the micro-pendant drop and sessile drop

techniques. Slattery and Chen's refinements allow utilizing the maximum diameter and length of the drop, which are the easiest dimensions to be measured by an experimentalist. Detailed results and drop shape factors were calculated and were given in terms of these easily measurable dimensions.

The theory of the spinning drop method is based on the balance between the centrifugal forces and interfacial forces acting upon the drop. When a fluid drop (gas bubble or liquid drop) is injected into a liquid of higher density contained in a rotating horizontal tube, it becomes subject to elongation along its axis of rotation. The drop reaches an equilibrium elongation as the deformation forces, due to the applied centrifugal field, are balanced by the interfacial tension, Figure 12. If the density difference between the two fluid phases $\Delta\rho$, the diameter of the drop D , its length L and the rotation speed ω are measured, the interfacial tension is then calculated according to the following equation

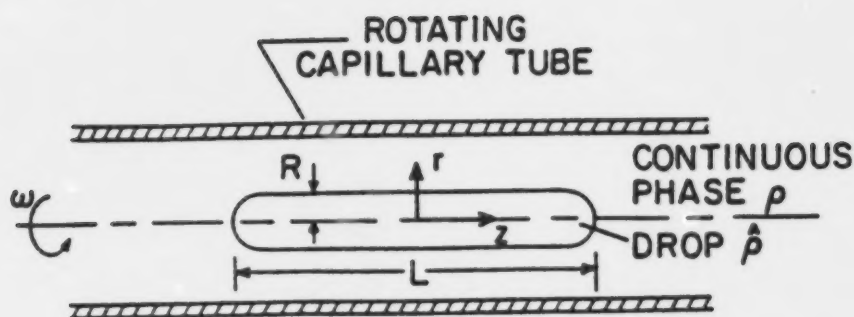
$$IFT = \frac{1}{32} \Delta\rho \omega^2 D^3 f(L/D) \quad \dots(1)$$

In this equation $f(L/D)$ is a shape factor which accounts for L/D effects associated with short drops ($L/D < 4$). For high rotation speeds and/or low interfacial tension, the length-to-diameter ratio may be greater than 4. Under such a condition, the interfacial tension equation is reduced to

$$IFT = \frac{1}{32} \Delta\rho \omega^2 D^3$$

For short drops, however, Slattery and Chen have given detailed tabulation of the value of the shape parameter as a function of maximum length-to-diameter ratio. Whenever L/D was less than 4, these values have been employed in the present study.

GEOMETRY



MEASUREMENTS REQUIRED: R, L, ω , and $\rho - \hat{\rho}$

DETERMINATION FROM:

$$\sigma = \frac{1}{4} \Delta \rho \omega^2 R^3 f(L/D) \quad , \quad (D = 2R)$$

WHEN $L > 5D$, $f(L/D) \approx 1$

FIGURE 12
DETERMINATION OF INTERFACIAL TENSION
BY THE SPINNING DROP METHOD

4.2 Measurement Procedure

All the interfacial tension measurements were carried out using a SITE LP-10 Spinning Drop Interfacial Tensiometer (EOR Inc., Houston, Texas). A description of the instrument and its capabilities has been reported in a number of publications, e.g. [37], [38], [39]. The design and development of this instrument has taken place at the Institute of Petroleum Engineering in Clausthal, W. Germany.

In addition to a connected temperature bath, the instrument consists of four major components: a spinning cell, a tilting base, an electronic control box, and a microscope arrangement. Details of the parts of the instrument will not be given here; but may be found in the instrument operating manual [40]. For easy reference, however, the set-up of the SITE LP-10 Spinning Drop Tensiometer is shown in Figure 13.

A number of points, specific to the instrument used in this study, are important to mention here:

- . The eyepiece scale, of the microscope arrangement, is only relative and must be calibrated against a true scale. The value obtained will vary slightly from one microscope to another, even for the same standard 63 mm objective lens. We have calibrated our microscope vernier scale against a very accurate optical reticle. A value of 349 vernier scale units/cm was obtained. This value was consistently used in all the IFT calculations.
- . Because of light refraction effects, due to the curved surface of the rotating capillary, the drop diameter obtained with the microscope micrometer in vernier scale units is only an "apparent" dimension. The "actual" drop diameter must be obtained from the measured apparent value either using a calibration factor, or via light refraction calculations. The latter approach was used in our calculations by taking into account the refractive indices of the continuous phase in the rotating tube and the thermal oil surrounding the rotating capillary. The refractive index of the continuous phase was always taken as 1.333 (equal to that of water). The thermal oil used throughout

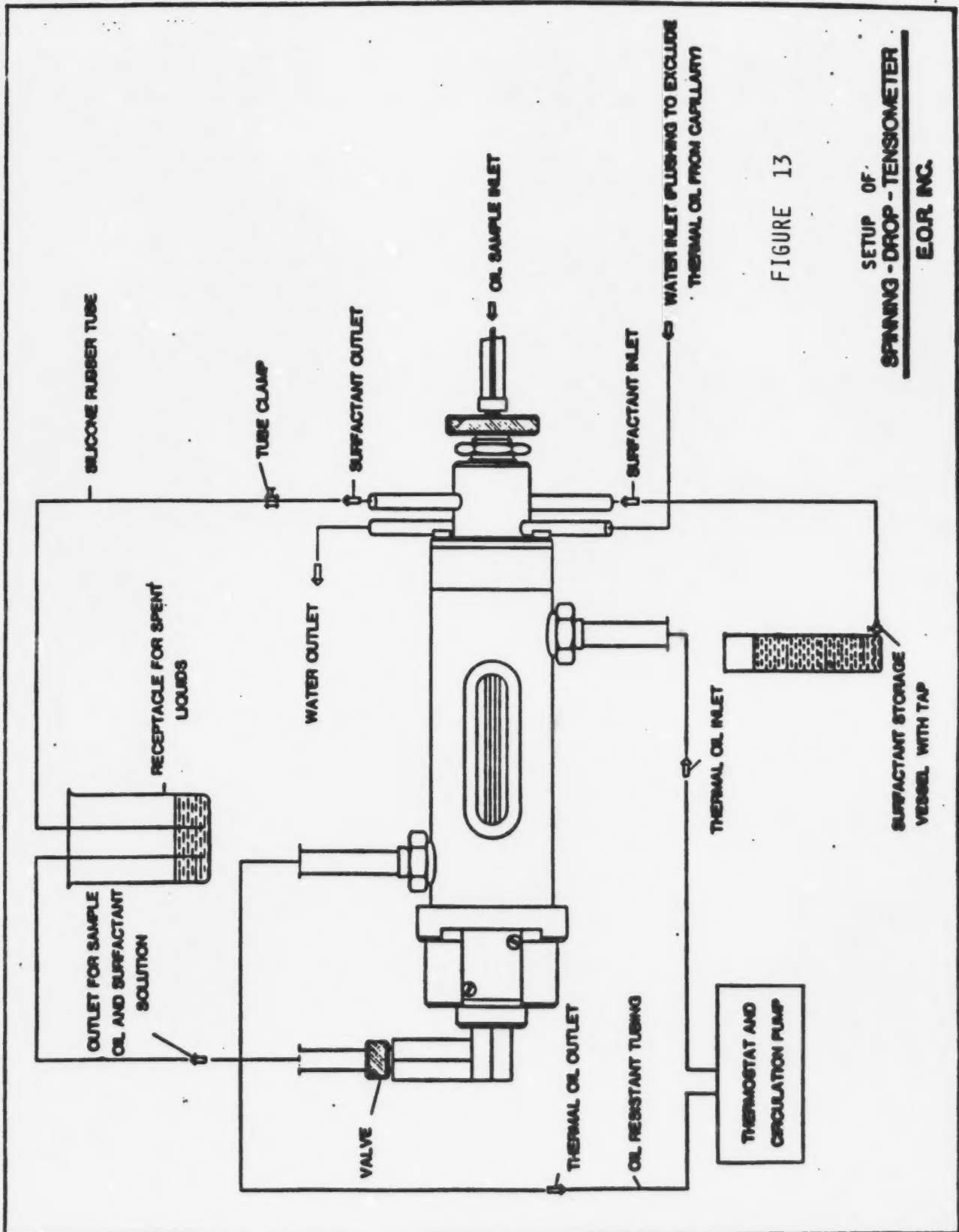


FIGURE 13

SETUP OF
SPINNING-DROP-TENSIONOMETER
E.O.R. INC.

the course of the measurements was Dow Corning "200 Fluid 50 cs" silicone oil, which has a refractive index of 1.4. From these values and for small drop diameters, the actual diameter D was calculated from the apparent diameter D_{app} as

$$D = 1.05 D_{app} \quad \dots(2)$$

As clearly shown by Eq. 1, in the determination of interfacial tension by the spinning drop method, one must measure the following quantities: the density of the continuous phase, density of the oil phase, rotation speed, the centre diameter of the spinning drop, and length of the spinning drop. The densities of the two phases were independently measured, as given in the characterization section (Sec. 2). The rotation speed was directly provided by the instrument's internal photo-switch/RPM readout arrangement; and was independently checked with a strobe light unit. The dimensions of drop, used for IFT calculations, were always measured as soon as the drop reached its equilibrium shape. The time to achieve this shape varied from a few seconds to about half an hour, depending on the system. It generally took longer, to achieve the equilibrium shape, for low IFT systems and vice versa.

After finishing the measurements on a particular system, it was found very important to thoroughly flush and completely clean not only the rotating tube but also the connecting alkali solution pipe-work. Thus, several hundred mL of the new alkali solution were used to flush the entire system. We have also, always, followed the practice of starting out with the lower alkaline concentration system, then flushing and cleaning with the next higher concentration to be studied. The pH of the flushing solution was always checked in the feed and effluent. Matching the two pH's was the criterion applied before taking actual IFT measurements on a new system.

4.3 IFT Measurement Results and Discussion

As mentioned earlier, three Saskatchewan heavy oils (two Gulf W. Edam crudes and a Saskoil Buffalo Coulee crude) have been examined in the IFT study. For each of the W. Edam oils, IFT measurements were carried out at both room temperature (nominal temperature of 20°C) and at a nominal temperature of 30°C. Seven different additive concentrations, ranging from zero (brine with no additive) to 40.0 g/L, were employed. Again, sodium hydroxide and sodium orthosilicate (METSO 200) were the two additives applied. For the Buffalo Coulee oil, IFT measurements were carried out only at room temperature. In the case of this oil, the continuous phases considered included distilled water, brine, 0.1 g/L and 10.0 g/L of each of the two alkaline additives in brine. Moreover, the effect of salinity on IFT was examined by repeating the set of W. Edam oil (5-30-48) measurements using NaOH solutions in distilled water instead of brine.

The results of the study are given in Figures 14 to 18, and Tables 9 to 12. The figures and tables show the effect of additive concentration, pH of additive solution, salinity of solution as well as temperature on the IFT of Saskatchewan oils. These results, and associated observations, are discussed in the following.

The results indicate that sodium hydroxide and sodium orthosilicate have comparable effects in reducing the interfacial tension of all three Saskatchewan oils. Thus, with only a few exceptions, the measured IFT of each of the three crudes with sodium hydroxide solution was very close to its value with sodium orthosilicate, at the same alkaline additive concentration. This result is not unexpected; for previous studies, e.g. [9], have shown that NaOH and Na_4SiO_4 were essentially equivalent in reducing the IFT of a number of crudes, particularly in the absence of hardness ions. In our prepared synthetic formation water (brine solution) only NaCl was used, with no Ca or Mg ions present.

FIGURE 14
EFFECT OF CONCENTRATION ON IFT (20 C)

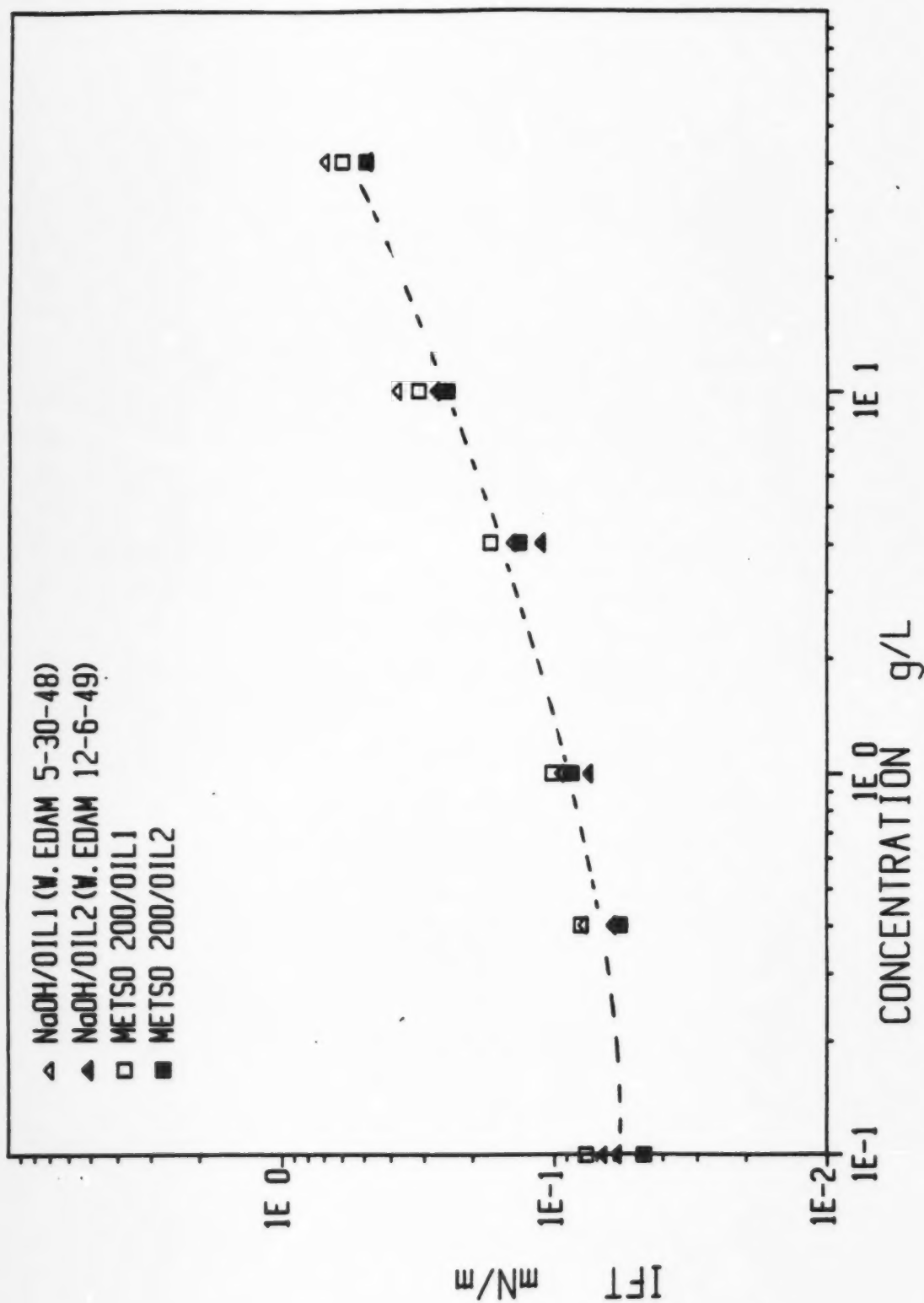


FIGURE 15
EFFECT OF pH ON IFT (20 C)

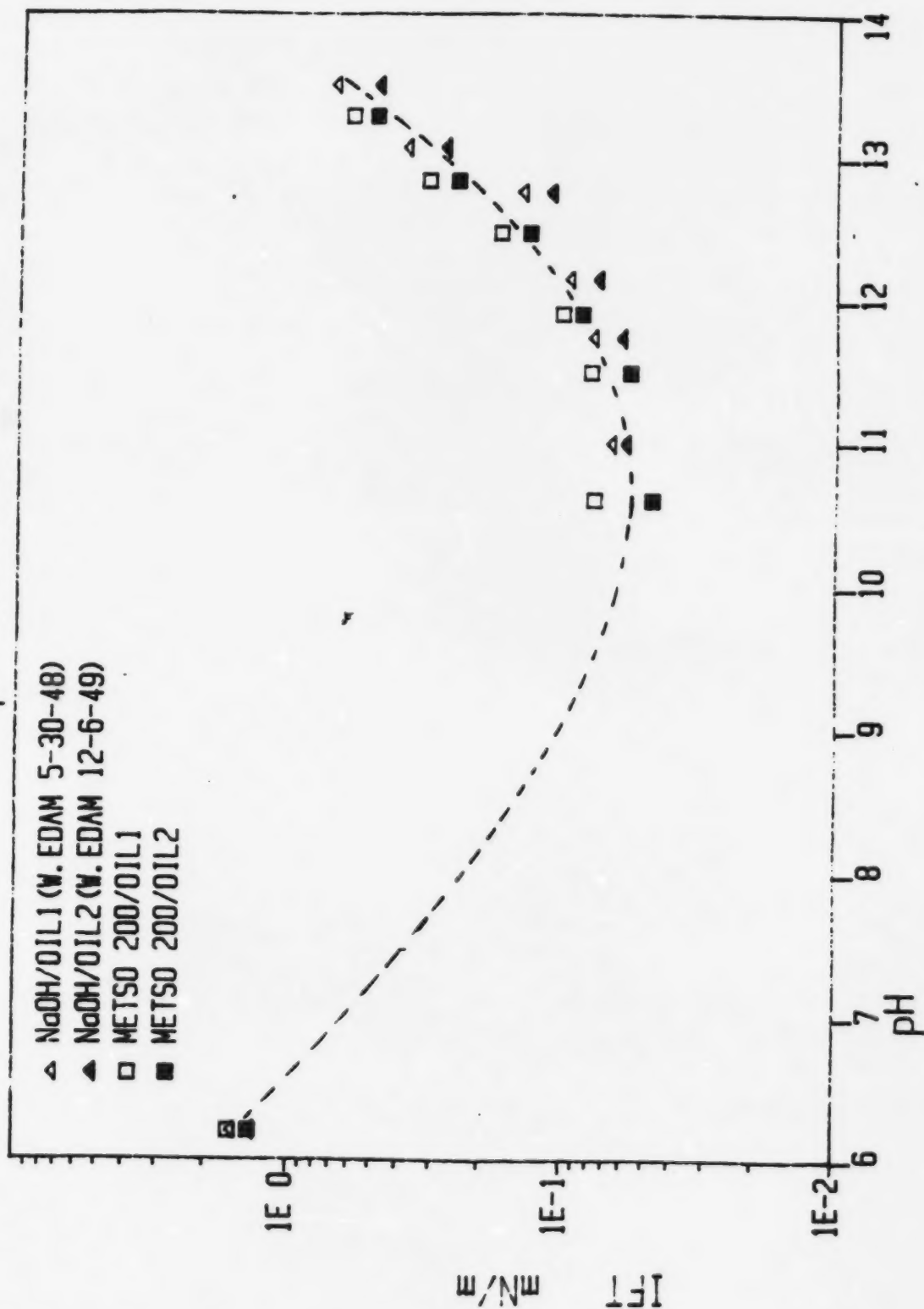


FIGURE 16
EFFECT OF CONCENTRATION ON IFT (30 C)

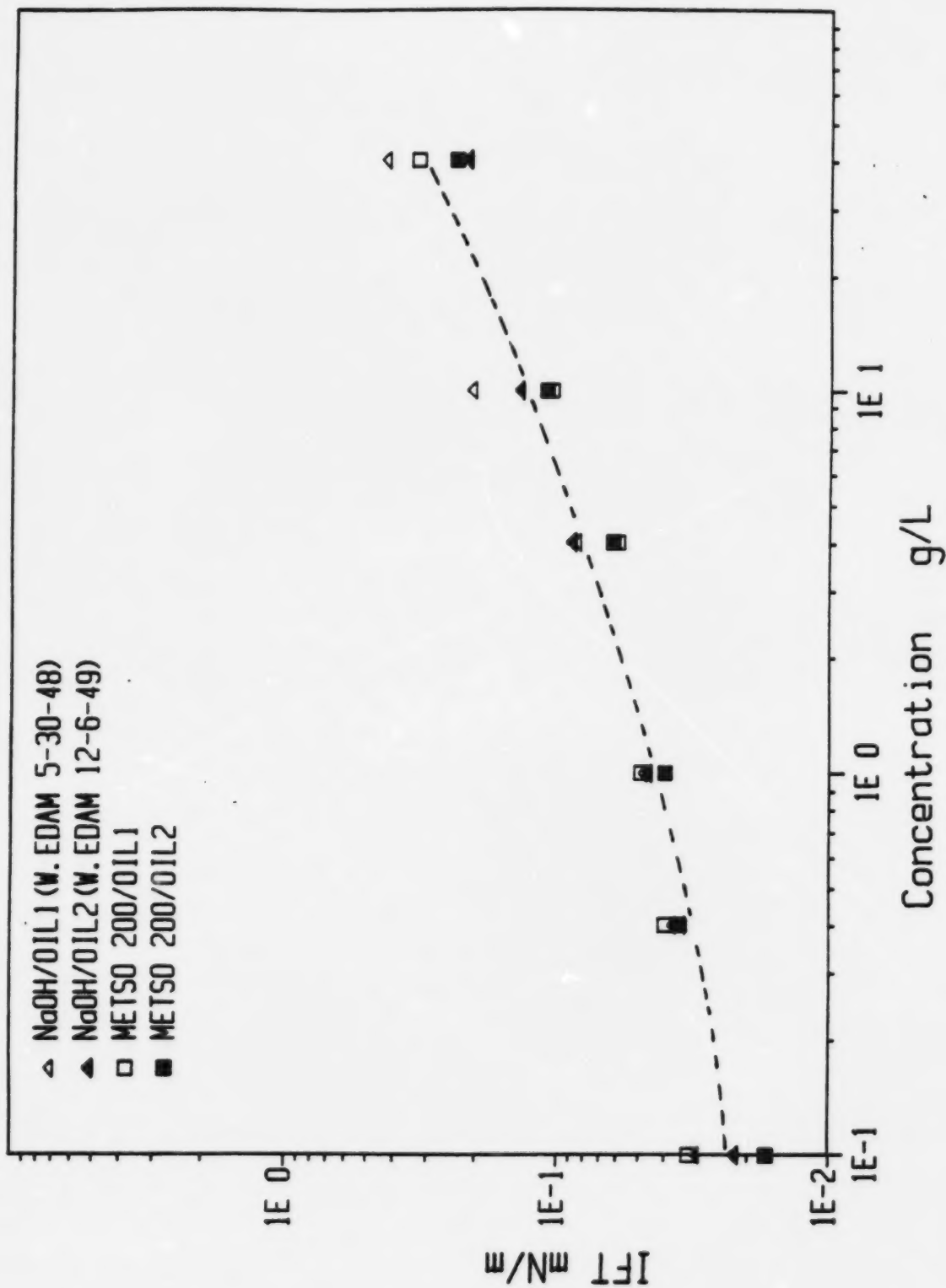


FIGURE 17
EFFECT OF pH ON IFT (30 C)

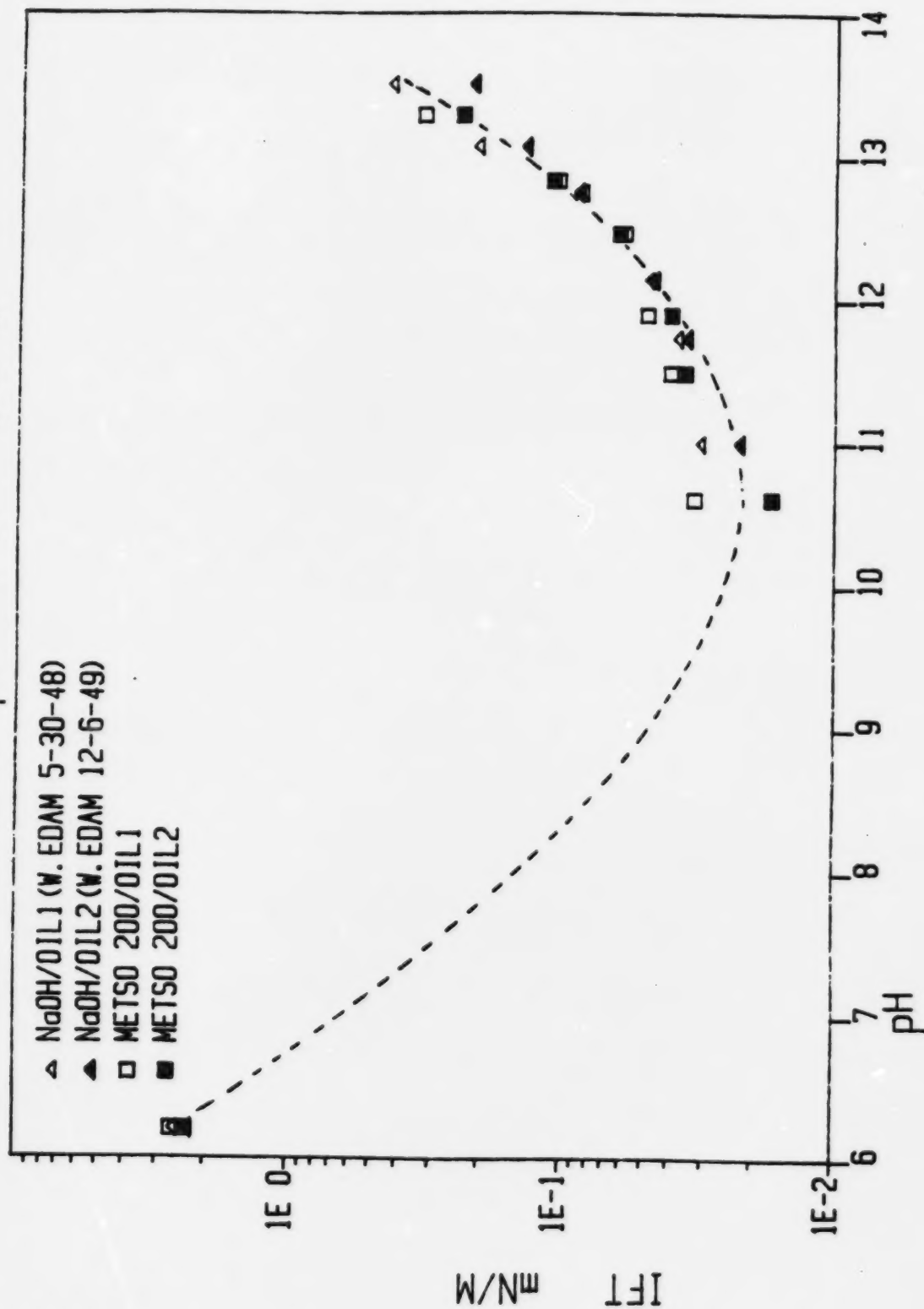


FIGURE 18
Effect of Concentration on IFT

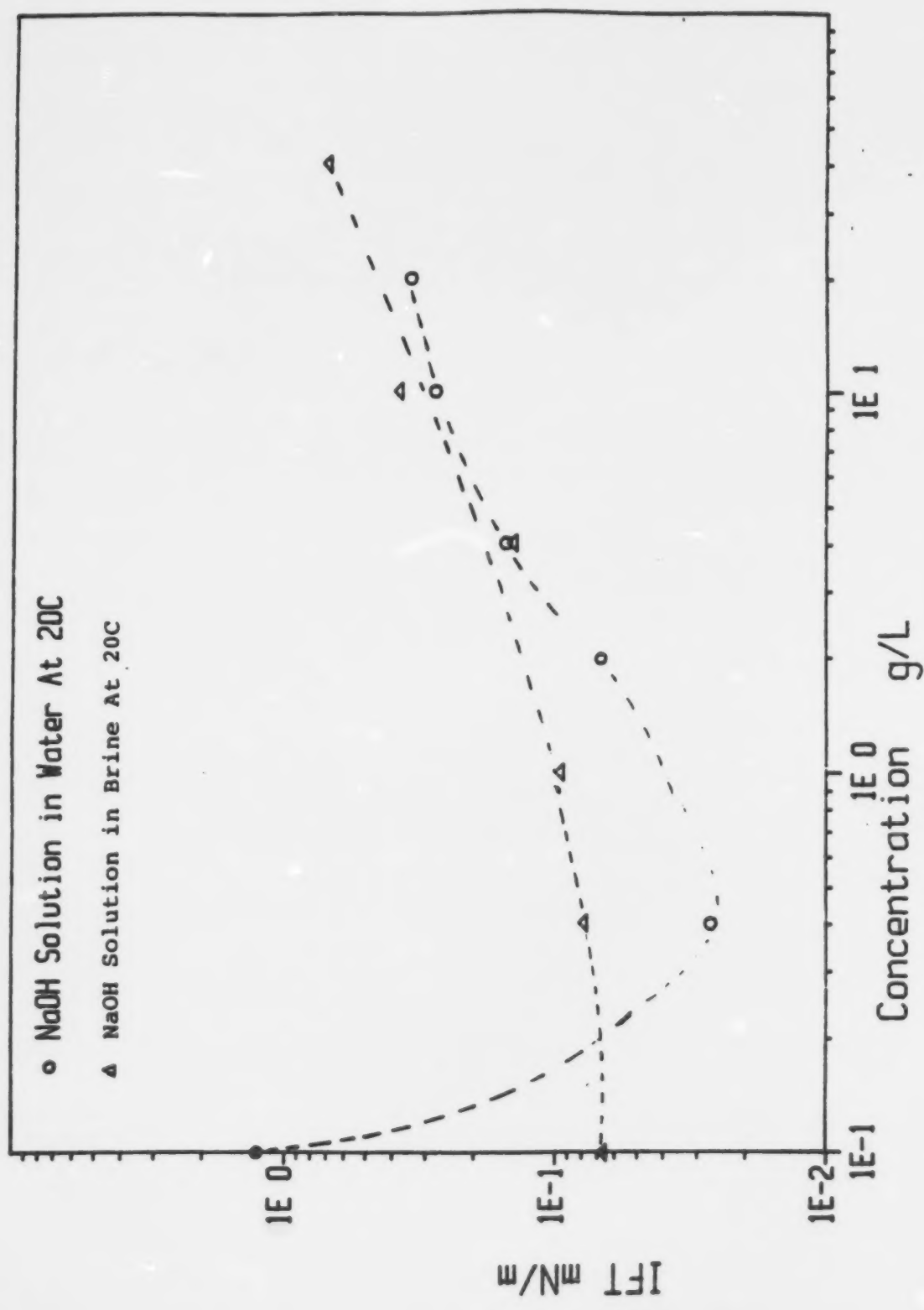


TABLE 9

IFT OF W. EDAM OILS/NaOH SOLUTIONS IN BRINE

NaOH Conc g/L	pH	IFT mN/m (W. Edam 5-30-48)		IFT mN/m (W. Edam 12-6-49)	
		20°C	30°C	20°C	30°C
0.1	11.01	0.068	0.031	0.060	0.023
0.4	11.74	0.081	0.038	0.062	0.035
1.0	12.14	0.097	0.048	0.075	0.046
4.0	12.75	0.144	0.086	0.115	0.090
10.0	13.07	0.380	0.210	0.284	0.140
40.0	13.50	0.725	0.432	0.496	0.220
Brine	6.2	1.58	2.6	1.34	2.31

TABLE 10

IFT OF W. EDAM OILS/METSO 200 SOLUTIONS IN BRINE

METSO Conc g/L	pH	IFT mN/m (W. Edam 5-30-48)		IFT mN/m (W. Edam 12-6-49)	
		20°C	30°C	20°C	30°C
0.1	10.61	0.075	0.032	0.047	0.017
0.4	11.50	0.078	0.040	0.057	0.035
1.0	11.90	0.103	0.049	0.085	0.040
4.0	12.47	0.172	0.060	0.133	0.063
10.0	12.83	0.310	0.106	0.250	0.110
40.0	13.28	0.604	0.330	0.500	0.235

TABLE 11

IFT OF W. EDAM OIL (5-30-48)/NaOH SOLUTIONS
IN DISTILLED WATER

<u>NaOH Conc</u> <u>g/L</u>	<u>pH</u>	<u>IFT mN/m</u>
0.1	11.1	1.28
0.4	11.8	0.026
2.0	12.5	0.068
4.0	12.85	0.153
10.0	13.05	0.279
20.0	13.4	0.344
Water	6.3	3.11

TABLE 12

INTERFACIAL TENSION OF BUFFALO COULEE (SASKOIL) OIL
IN COMPARISON WITH GULF W. EDAM OIL

Solution	IFT (at 20°C) mN/m		
	W. Edam <u>5-30-48</u>	W. Edam <u>12-6-49</u>	<u>Saskoil</u>
Distilled Water	3.11	--	1.12
Brine	1.58	1.34	0.65
0.1 g/L NaOH in Brine	0.068	0.060	0.024
10.0 g/L NaOH in Brine	0.38	0.28	0.11
0.1 g/L Na ₄ SiO ₄ in Brine	0.075	0.047	0.048
10.0 g/L Na ₄ SiO ₄ in Brine	0.31	0.25	0.12

Comparing the IFT of the three different crudes, it is clear that the two W. Edam oils have very similar characteristics. This includes not only the various trends - with concentration, pH and temperature - but also the magnitude of IFT value at identical conditions. The Buffalo Coulee oil, on the other hand, showed significantly lower IFT than the W. Edam crudes, at equivalent conditions of alkaline additive concentrations. Referring to the characterization section (Sec. 2), the Buffalo Coulee and the W. Edam oils were found to exhibit comparable acid numbers. This confirms that a lower interfacial tension is not necessarily correlated with a higher acid number; a view shared with most recent literature [4].

Regarding the effect of temperature, the two W. Edam crudes exhibited a decrease in IFT with an increase in temperature from 20°C to 30°C. The decrease of IFT with increasing temperature is in agreement with most studies in the literature [41,42]. Strictly speaking, however, the temperature effect depends on the characteristics of the oil and surfactant involved, as well as the range of temperatures considered. Burkowsky et al [37-39], for example, showed a minimum type behaviour of IFT, for a number of oil-surfactant systems; with the IFT minima occurring in the range of 50 - 70°C. In the case of brine with the W. Edam oils, we have observed an increase of IFT with temperature, Table 9. Hjelmeland and Larrondo [43] found the interfacial tension between crude oil, from an Alberta carbonate reservoir, and brine to show an increase with temperature under anaerobic conditions. At aerobic conditions, however, they reported that IFT decreased with temperature.

The effect of alkaline additive concentration on interfacial tension has been closely examined for the W. Edam oils. The results show that IFT falls rapidly to a minimum in the presence of low concentration of the alkaline agent in brine (either sodium hydroxide or sodium orthosilicate at 0.1 g/L brine). IFT, then, begins to increase as the concentration of the alkaline additive increases. This pronounced minimum is clearly illustrated in the IFT-pH figures 15 and 17. The log-log scale of the IFT-concentration figures does not permit appropriate illustration of this minimum behaviour.

Numerous studies in the literature have shown similar trends of IFT with alkali concentration [9, 10, 46]. Probably the most complete explanation of this minimum IFT behaviour and the adverse effect of excess caustic concentration is that given by Chan and Yen [44]. They proposed a simple model based on the equilibrium between three reactions; namely:

- the dissociation of naturally occurring acids at alkaline pH to generate an interfacial active species,
- the deactivation of the active species with the Na^+ (from NaCl or NaOH ...) to form undissociated salt,
- dissociation of water.

According to the model, the sudden drop corresponds to the ionization of the R-COOH acid species to the active R-COO⁻ species at high pH. Further increase in alkali concentration beyond this point causes the concentration of active species at the interface, as calculated from the equilibrium and mass balance equations, to decrease. This, in turn, causes the interfacial tension to increase.

The presence of NaCl in the aqueous phase also plays an important role in lowering the interfacial tension. In Figure 18 it is clear that, in the absence of NaCl, a higher caustic concentration is required to reduce IFT to the same minimum levels. The effect of the presence of sodium chloride in reducing the amount of NaOH required to reach a given reduced level of IFT has also been long recognized [1]. The model of Chan and Yen [44] gives an explanation of this behaviour; and further suggests that excessive salt concentration causes IFT to increase, as does excessive NaOH concentration.

Examining the effect of alkali concentration on interfacial tension, illustrated in Figures 14 and 16, suggested that a simple relationship between log IFT and log C (C is the alkaline additive concentration) may exist. Thus the following second degree polynomial correlation was adopted

$$\log \text{IFT} = a + b. \log C + c(\log C)^2 \quad \dots(3)$$

A non-linear regression routine, based on Marquardt's method which combines the Gauss technique with the method of steepest descent, was employed to correlate the experimental data according to the above model. Good correlations were obtained, as indicated by a small variance of residuals and a small 95% confidence interval on the parameter estimates in each case. Table 13 gives the least squares estimates of the parameters a, b and c corresponding to each temperature and combination of additive with each of the two W. Edam oils. The table also lists the variance of residuals calculated for each correlation.

If one assumes the pH to be roughly proportional to log C, then the following correlation of IFT with pH would be possible

$$\log \text{IFT} = q + r. \text{pH} + s. \text{pH}^2 \quad \dots(4)$$

Again the data was correlated according to the above equation. In this case the brine pH and IFT measurements were also included in the correlated data. The correlations were still good, reflecting the pronounced minimum of IFT vs. pH. Table 14 gives the least squares estimates of the parameters q, r and s and variance of residuals for each correlation.

TABLE 13

CORRELATION OF IFT WITH ALKALI CONCENTRATION

$$\log \text{IFT} = a + b \cdot \log C + c \cdot (\log C)^2$$

<u>Temp</u> <u>°C</u>	<u>Alkali</u>	<u>W. Edam Oil</u>	<u>a</u>	<u>b</u>	<u>c</u>	<u>V.R.</u>
20	NaOH	5-30-48	-2.309	0.318	0.066	0.038
20	NaOH	12-6-49	-2.544	0.286	0.066	0.038
30	NaOH	5-30-48	-2.978	0.372	0.063	0.025
30	NaOH	12-6-49	-2.988	0.379	0.010	0.008
20	METSO 200	5-30-48	-2.253	0.292	0.054	0.009
20	METSO 200	12-6-49	-2.511	0.347	0.042	0.008
30	METSO 200	5-30-48	-3.154	0.258	0.074	0.026
30	METSO 200	12-6-49	-3.209	0.386	0.021	0.022

TABLE 14

CORRELATION OF IFT WITH pH

$$\log \text{IFT} = q + r. \text{pH} + s. \text{pH}^2$$

<u>Temp</u> <u>°C</u>	<u>Alkali</u>	<u>W. Edam Oil</u>	<u>q</u>	<u>r</u>	<u>s</u>	<u>V.R.</u>
20	NaOH	5-30-48	20.52	-4.567	0.230	0.075
20	NaOH	12-6-49	19.65	-4.478	0.219	0.072
30	NaOH	5-30-48	26.15	-5.803	0.281	0.047
30	NaOH	12-6-49	24.19	-5.355	0.256	0.005
20	METSO 200	5-30-48	19.62	-4.458	0.221	0.029
20	METSO 200	12-6-49	20.99	-4.823	0.240	0.014
30	METSO 200	5-30-48	24.45	-5.394	0.259	0.070
30	METSO 200	12-6-49	26.15	-5.837	0.283	0.020

5. SYNTHETIC CORE DISPLACEMENT

Interfacial tension measurements under idealized conditions, as reported in the previous sections, may not accurately represent the dynamic field situation. Under field conditions, surfactant is likely to be continuously generated in situ, and depleted by adsorption or reaction with various ions. Displacement studies, in synthetic cores, give a better approximation of these dynamic interactions, and provide a better estimation of oil recovery improvement due to alkali addition versus plain waterflooding. The use of synthetic cores avoids such complicating factors as the presence of clays, heterogeneous pore size, permeability variations and wettability changes.

Two sets of displacement runs have been conducted; each in accordance with a 2^3 factorial design of experiments. The only difference between the two sets of experiments is that W. Edam oil (5-30-48) was used in the first, while Buffalo Coulee oil was used in the second. The three factors considered in each set of experiments, each at two levels, were the type of alkaline additive, the concentration of alkali in the injection fluid, and the displacement flow rate. Again, the two additives considered were sodium hydroxide and sodium orthosilicate. The concentration levels, of each of the two additives, were 0.1 and 10 g/L. Two nominal flow rates of 180 g/h and 280 g/h were used in each set of experiments.

5.1 Displacement Experiments, Set-Up and Procedure

All the synthetic core displacement experiments were carried out using sand-packs saturated with one of the two Saskatchewan oils, W. Edam 5-30-48 or Buffalo Coulee, while brine was always at the irreducible connate level. Well mixed Ottawa sand ASS #35 was packed in 28 in. long, 1 in. O.D., 316 SS (ASTM A-213) tubing. Several identical core holders were used; each packed with 492 ± 6 g of the same Ottawa sand. A standardized dry packing technique was consistently used. The average porosity and permeability of these synthetic cores were 0.35 and 44 darcy, respectively. All experiments

were carried out at room temperature, while a back pressure of 500 psig was maintained at the system collection point. The pressure drop across the core and the inlet pressure were monitored throughout each run. The injection rate was kept constant in each run, at a value as close as possible to the decided nominal feed rate. The displaced product was collected at five minute intervals at the beginning of each run, and at longer intervals later in the run. The entire product, collected at the end of each time interval, was analyzed for water/oil content.

Excluding the specifics of each run (i.e. additive type and concentration, displacement rate, and oil involved), all the displacement experiments followed the same general procedure. This procedure is outlined in the following

- The sand core was saturated with water at room temperature.
- Several pore volumes of oil, heated to about 65°C to facilitate injection, were continuously fed to displace the water in the core. Oil injection was continued until the water saturation was reduced to the connate level (determined to be approximately 10%).
- The core section was isolated, using the inlet and outlet valves shown in Figure 19. The core was then by-passed and the oil in the inlet and outlet pipework was flushed with solvent. Flushing continued until all connecting pipework was clean and free of oil. With the core still isolated, the solvent in the connecting inlet, outlet, and by-pass piping was completely displaced with brine or alkali solution depending on the condition of the run. The process of cleaning the inlet and outlet piping, to the core, was necessary for accurate monitoring of the oil displacement, and facilitated a convenient calculation of oil recovery as a function of fluid injection.
- The core inlet and outlet valves were then opened, the core by-pass was closed, and fluid injection was started at the pre-specified constant rate.
- The displaced product was collected, as earlier indicated, and analyzed using the standard Dean-Stark method.
- The run was terminated after injecting up to 10 pore volumes of fluid.

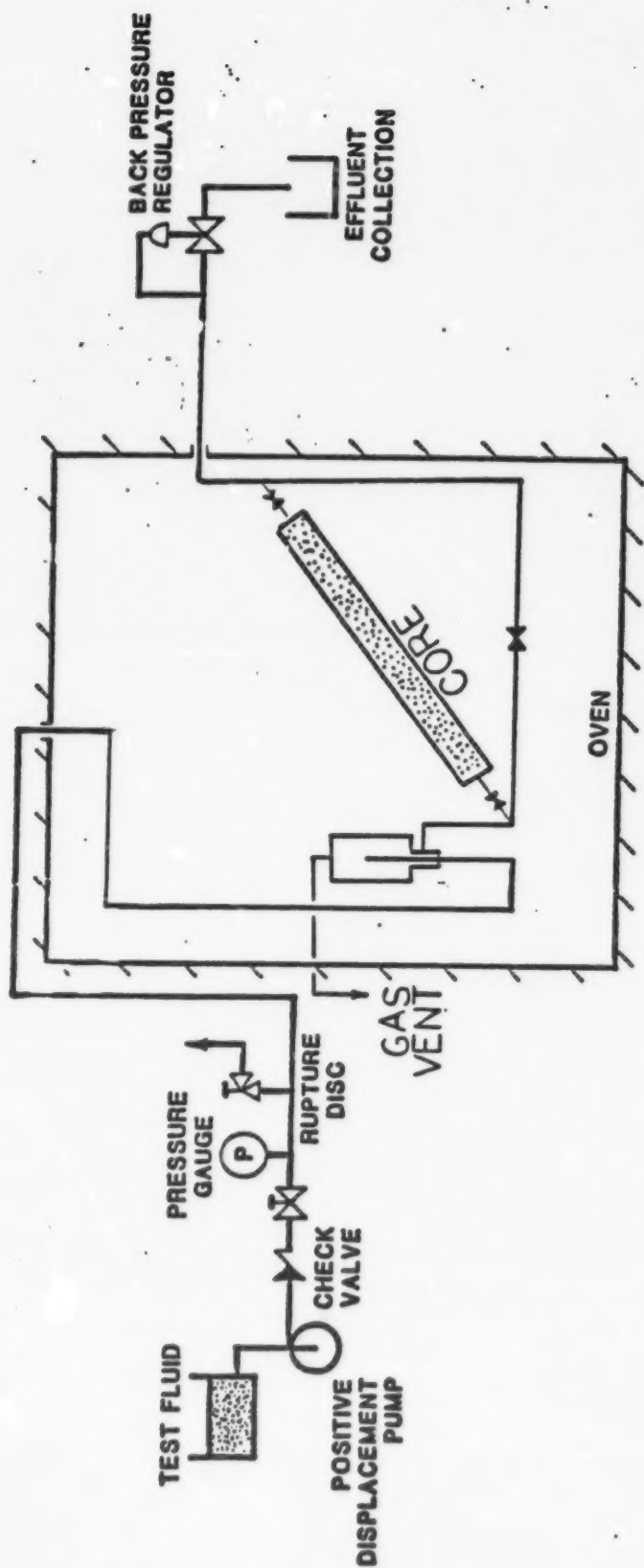


FIGURE 19
SYNTHETIC CORE DISPLACEMENT SET-UP

5.2 Synthetic Core Displacement Results and Discussion

The raw data of the W. Edam oil set of displacement experiments are tabulated in Appendix 1, Tables A1 to A10. For each run, the corresponding table includes the designated product sample number, the time at which the sample was collected, the feed scale reading, total weight of product collected, and the weight of water in each produced sample. The water content in each produced fluid sample was determined by the method of Dean-Stark, while the oil content was calculated by difference. In the tables, a correction was made to allow for excluding the volume of fluid retained in the outlet pipework which amounted to approximately 12 mL. This volume, therefore, was subtracted from the volume of water produced in the first sample.

Designation, conditions, as well as a summary of the oil recovery and water-oil ratio results of the W. Edam oil runs are given in Table 15. The tabulated oil recovery, given as a fraction of the original oil in the core (normally denoted as hydrocarbon pore volume HCPV), and the cumulative water-oil ratio are interpolated from the recovery data at exactly 6 pore volumes of fluid injected (PV was determined to be 110 mL for our system, while HCPV was 99.4 mL). In addition to the set of alkaline flooding factorial experiments, the table includes two initial base runs using brine and distilled water as the injection fluids. Figures 20 and 21 summarize the oil recovery and water-oil ratio results of all the W. Edam oil experiments including the two initial base runs.

The results indicate a favourable effect of both the sodium hydroxide and sodium orthosilicate alkaline additives in enhancing oil recovery and lowering water-oil ratios. The incremental increase in oil recovery due to alkaline fluid injection, over distilled water or brine flooding, amounts to over 0.25 HCPV in some of the cases. A decrease in water-oil ratio of comparable magnitude may be also observed. It may be further observed in Figures 20 and 21 that the results of all the runs in the factorial set of alkaline flooding experiments are fairly close to each other, in spite of the differences in feed rates and additive type and concentration. Analysis of variance of this set of factorial experiments, however, led us to a number of most interesting findings about the data.

TABLE 15

W. EDAM OIL DISPLACEMENT EXPERIMENTS

<u>Run</u>	<u>Experimental Conditions*</u>	<u>% Oil Recovery (@ 6 PV Inj.)</u>	<u>WOR (@ 6 PV Inj.)</u>
Base Runs			
133-1	182 g/h distilled water	46	12.84
133-2	189 g/h brine	46	12.70
Set of Factorial Experiments			
133-5	183 g/h of 0.1 g/L NaOH soln.	66	8.66
133-6	282 g/h of 0.1 g/L NaOH soln.	74	8.00
133-7	159 g/h of 10 g/L NaOH soln.	64	8.90
133-8	269 g/h of 10 g/L NaOH soln.	68	8.69
133-9	170 g/h of 0.1 g/L Na ₄ SiO ₄ soln.	68	8.66
133-10	283 g/h of 0.1 g/L Na ₄ SiO ₄ soln.	71	8.19
133-11	179 g/h of 10 g/L Na ₄ SiO ₄ soln.	62	9.57
133-12	289 g/h of 10 g/L Na ₄ SiO ₄ soln.	66	8.95

* All experiments carried out at room temperature, under confining back pressure of 500 psig, using 490 $\pm$ 5 g of well mixed Ottawa sand (ASS #35) packed in 71 cm long, 2.2 cm dia. cores.

FIGURE 20
OIL RECOVERY, W. EDAM
OIL DISPLACEMENT EXPERIMENTS

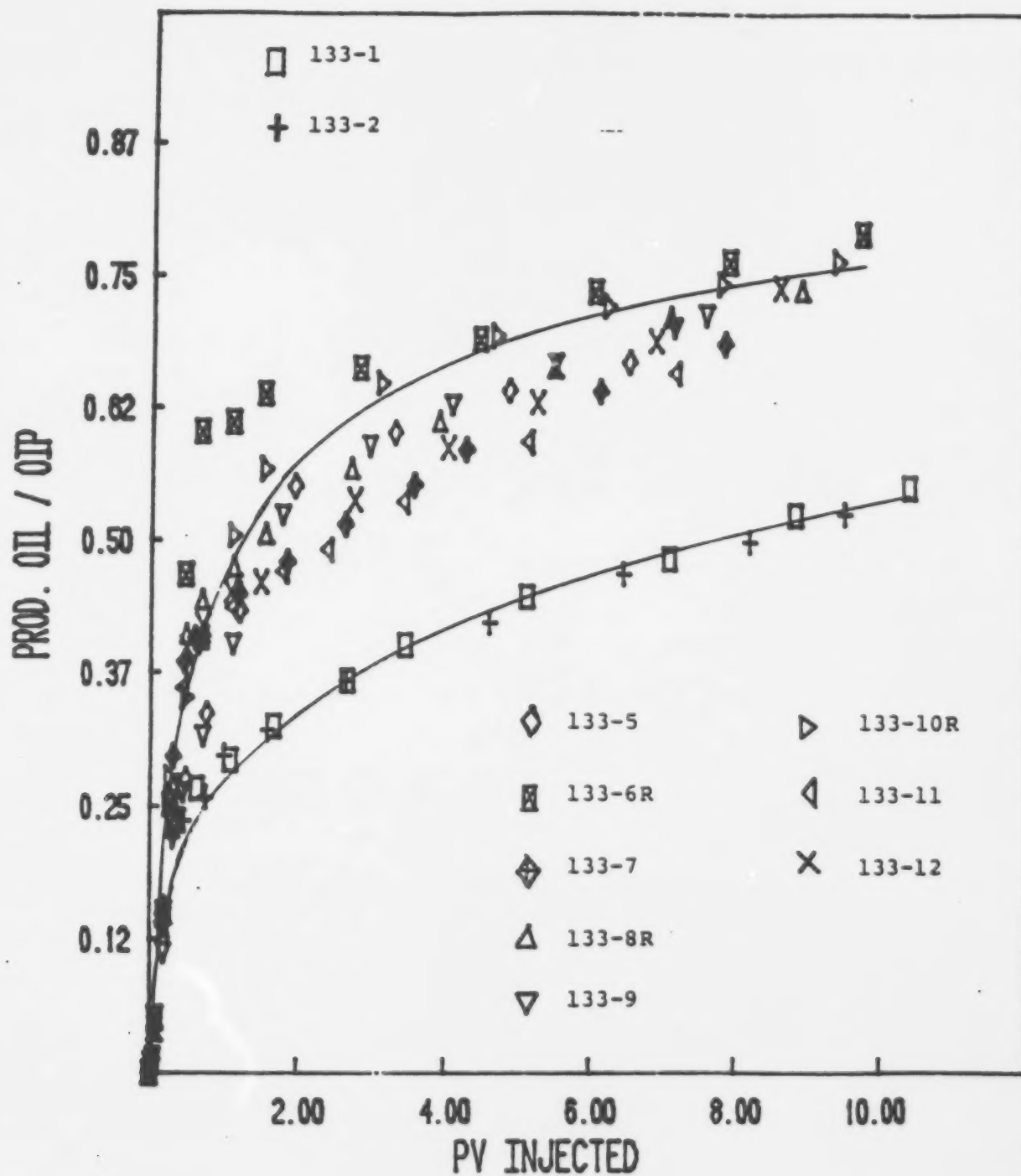
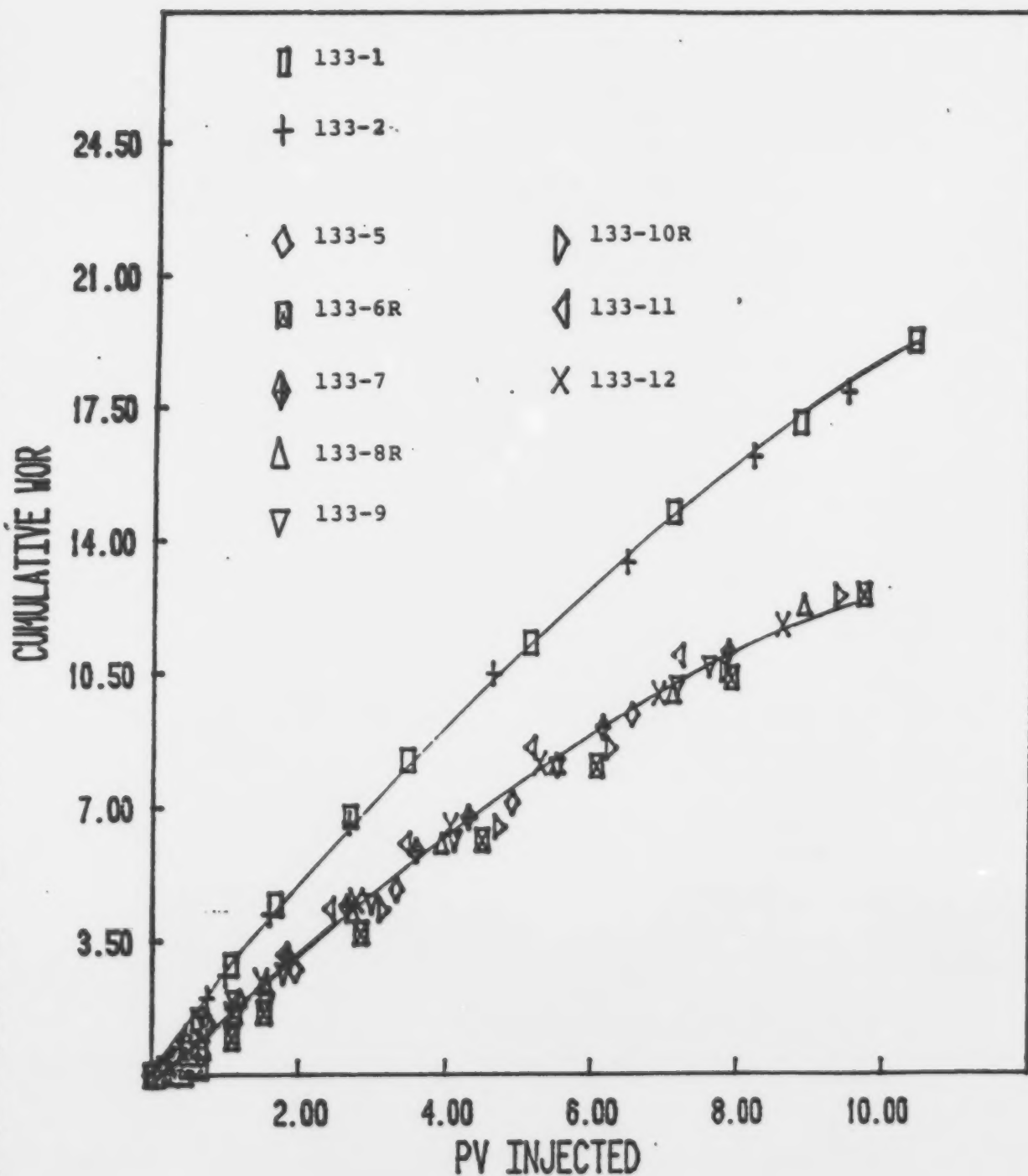


FIGURE 21
WATER-OIL RATIO, W. EDAM
OIL DISPLACEMENT EXPERIMENTS



The analyses of variance (W. Edam oil) are given in Tables 16 and 17, on the basis of the oil recovery and water-oil ratio results respectively. The two tables reveal that the effect of feed rate and additive concentration are significant at the 99 and 95% confidence levels. The effect of additive type, on the other hand, was not found to be significant. The analysis of variance based on oil recovery and on water-oil ratios are in good agreement, indicating the self consistency of the results. In carrying out the significance F-tests, the interactions were combined to obtain an estimate of the error variance which has been used as the error term. The F-values of the main effects (feed rate, additive type, and additive concentration) were then calculated and compared with the tabulated F-values $F_{5\%}$ and $F_{1\%}$, e.g. [47].

The finding that better recovery results are obtained at a concentration of 0.1 g/L, over 10 g/L, is in harmony with the minimum IFT observed in the spinning drop study at that concentration. As discussed earlier in the report, minimizing the interfacial tension results in such beneficial effects as emulsification and mobilization of oil ganglia. The present result, therefore, indirectly supports the presence of such useful mechanisms.

The finding of better recovery results at the higher feedrate, on the other hand, was interesting and somewhat surprising as it was not as obvious as the above result. There are, nevertheless, two main effects which can account for and explain the observed trend. First, while it has not been systematically studied in this project, a minimum in IFT at the initial contact of an alkaline additive with oil has generally been observed in numerous previous studies [37, 38, 39, 42, 43]. After this initial minimum, the interfacial tension is normally observed to increase with time to a higher equilibrium value. A high feedrate appears to take advantage of this phenomenon, as the displacement is carried out while IFT is at its minimum value. Low feedrates act in the opposite direction by increasing the contact time, and hence IFT, of the oil-alkaline fluid. The second factor, which explains the improved recovery at higher feedrates, is the increased capillary number. The capillary number is

TABLE 16

ALKALINE FLOODING 2³ FACTORIAL EXPERIMENT
WEST EDAM HEAVY OIL

ANALYSIS OF VARIANCE
(BASED ON OIL RECOVERY RESULTS)

Corrected Total Sum of Squares = 101.875
Degrees of Freedom = 7
Mean Square = 14.55

<u>Source of Variation</u>	<u>D.F.</u>	<u>S.S.</u>
Feed Rate	1	45.1
Additive Type	1	3.1
Additive Concentration	1	45.1
Rate x Type	1	3.1
Rate x Conc	1	1.1
Type x Conc	1	1.1
Rate x Type x Conc	1	3.1

Estimate of Error Variance = $(3.1 + 1.1 + 1.1 + 3.1)/4 = 2.1$

Test of Hypotheses Combining all ANOVA Interactions as an Error Term:

<u>Source</u>	<u>D.F.</u>	<u>S.S.</u>	<u>F Value</u>
Rate	1	45.1	21.5
Type	1	3.1	1.5
Conc	1	45.1	21.5

$F_{5\%}(1,4) = 7.71$, $F_{1\%}(1,4) = 21.2$

TABLE 17

ALKALINE FLOODING 2³ FACTORIAL EXPERIMENT
WEST EDAM HEAVY OIL

ANALYSIS OF VARIANCE
(BASED ON WATER-OIL RATIO RESULTS)

Corrected Total Sum of Squares = 1.613
Degrees of Freedom = 7
Mean Square = 0.230

<u>Source of Variation</u>	<u>D.F.</u>	<u>S.S.</u>
Feed Rate	1	0.48
Additive Type	1	0.16
Additive Concentration	1	0.85
Rate x Type	1	0.006
Rate x Conc	1	0.011
Type x Conc	1	0.068
Rate x Type x Conc	1	0.045

Estimate of Error Variance = $(0.006 + 0.011 + 0.068 + 0.045)/4$
= 0.033

Test of Hypotheses Combining all ANOVA Interactions as an
Error Term:

<u>Source</u>	<u>D.F.</u>	<u>S.S.</u>	<u>F Value</u>
Rate	1	0.48	14.77
Type	1	0.16	4.85
Conc	1	0.85	25.76

$F_{5\%}(1,4) = 7.71$, $F_{1\%}(1,4) = 21.2$

defined as the ratio of viscous to interfacial forces

$$\text{Capillary number} = \frac{\mu u}{\text{IFT}}$$

where μ is the viscosity of the flowing fluid and u is the Darcy velocity of the displacement front. An increase in the capillary number is generally believed to result in improved oil recovery [48]. Obviously an increase in feedrate, and correspondingly in the Darcy velocity, or a decrease in interfacial tension would result in an increase in the capillary number. The present result, therefore, demonstrates the usefulness of the concept of capillary number. Practically, floods in the field are generally operated at or near the maximum injection rate. This means that the displacement rate, u , is not generally significantly varied. Furthermore, the viscosity and porosity are fixed, showing once again the importance of IFT as the only parameter that can be modified to increase the capillary number.

The Buffalo Coulee crude, obtained from Saskoil, was used in the second part of this comparative synthetic core displacement study. The raw data of this set of experiments are given in Tables A11 to A21. The group of experiments include three brine and distilled water injection reference runs, and a set of 2^3 factorial experiments. The factors examined in the alkaline flooding experiments are identical with the previous W. Edam runs, and at exactly the same levels.

Designation, conditions, as well as a summary of the oil recovery and water-oil ratio results of the Buffalo Coulee oil runs are given in Table 18. Again, the tabulated oil recovery and the cumulative water-oil ratio are interpolated from the recovery data at exactly 6 PV of fluid injection. Figures 22 and 23 summarize the oil recovery and water-oil ratio results of all the Buffalo Coulee experiments including the three initial base runs.

The results exhibit trends similar to those observed for the W. Edam oil. Thus, both the sodium hydroxide and sodium orthosilicate injection fluids result in significantly higher

TABLE 18

BUFFALO COULEE OIL DISPLACEMENT EXPERIMENTS

<u>Run</u>	<u>Experimental Conditions</u>	<u>% Oil Recovery (@ 6 PV Inj.)</u>	<u>WOR (@ 6 PV Inj.)</u>
Base Runs			
133-21	178 g/h distilled water	52	11.9
133-22	183 g/h brine	58	10.4
133-23	277 g/h brine	54	11.3
Set of Factorial Experiments			
133-24	178 g/h of 0.1 g/L NaOH soln.	71	8.3
133-25	278 g/h of 0.1 g/L NaOH soln.	74	8.0
133-26	183 g/h of 10 g/L NaOH soln.	70	8.4
133-27	283 g/h of 10 g/L NaOH soln.	68	8.7
133-28	186 g/h of 0.1 g/L Na ₄ SiO ₄ soln.	72	8.2
133-29	276 g/h of 0.1 g/L Na ₄ SiO ₄ soln.	68	8.7
133-30	184 g/h of 10 g/L Na ₄ SiO ₄ soln.	73	8.0
133-31	283 g/h of 10 g/L Na ₄ SiO ₄ soln.	76	7.6

FIGURE 22
SASKOIL CRUDE DISPLACEMENT
EXPERIMENTS (OIL RECOVERY)

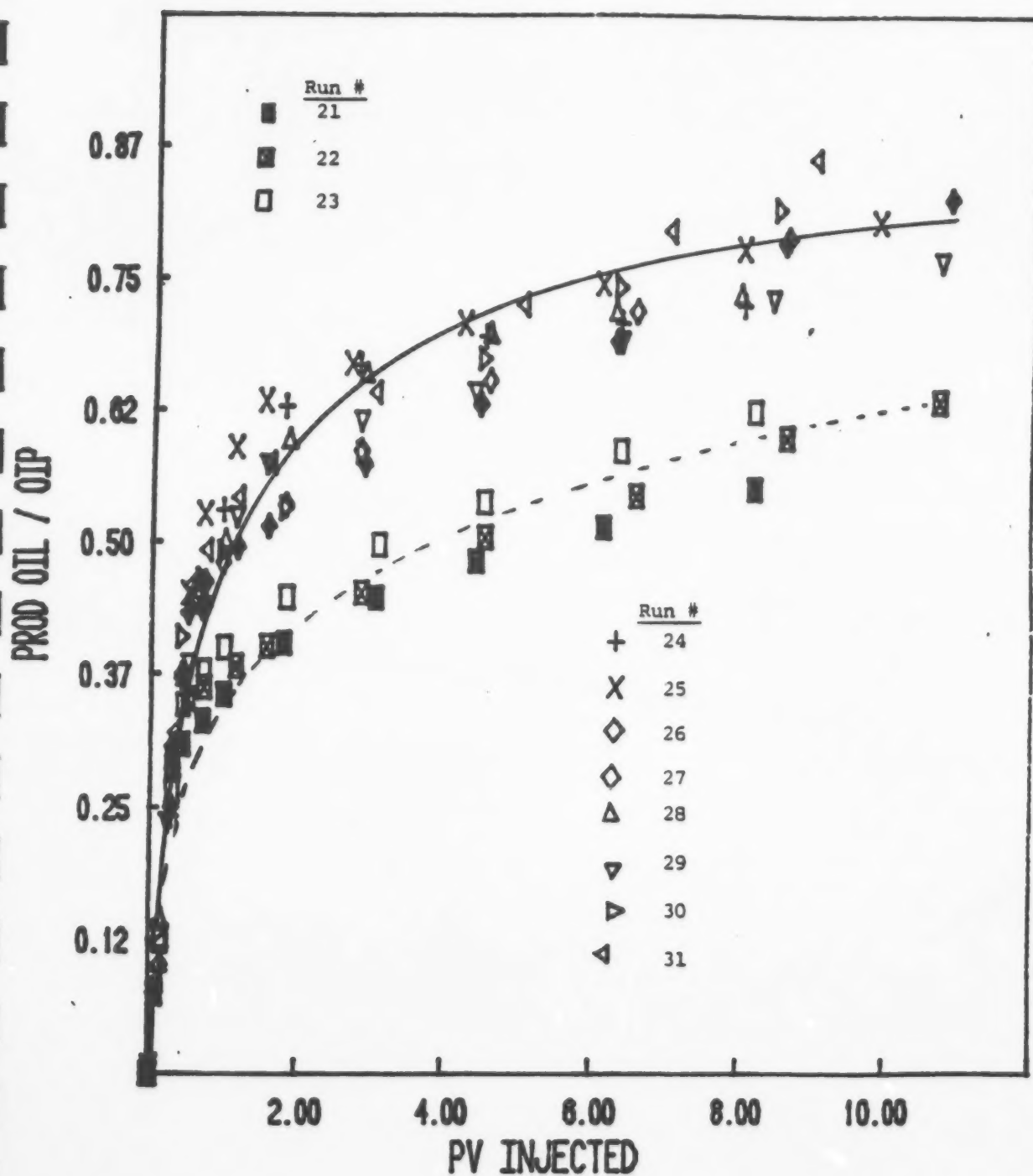
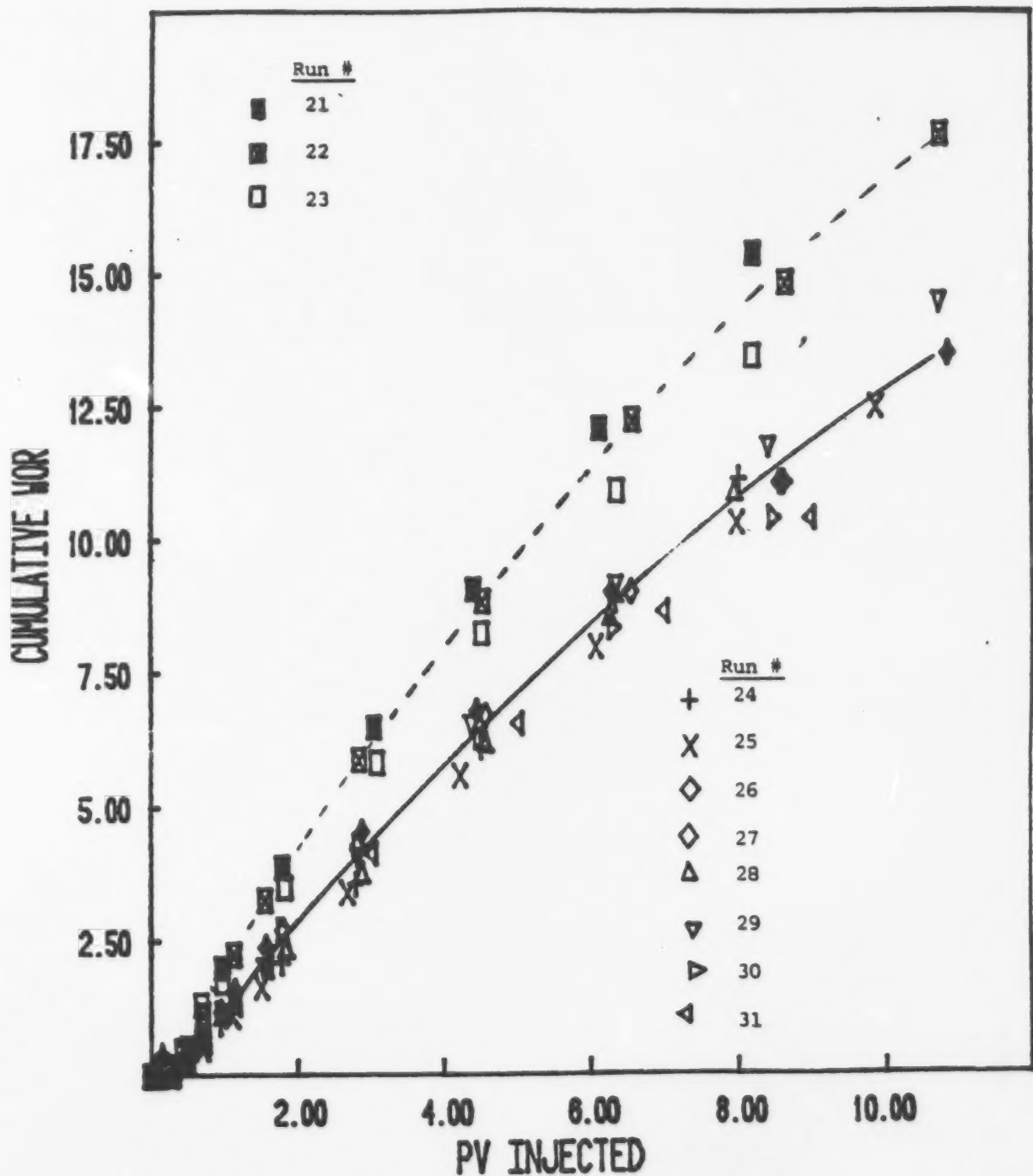


FIGURE 23
SASKOIL CRUDE DISPLACEMENT
EXPERIMENTS (WATER-OIL RATIO)



oil recovery and lower water-oil ratios, than distilled water or brine injection. In comparison with the W. Edam crude, nevertheless, the Buffalo Coulee shows somewhat higher oil recovery and lower water-oil ratios, i.e. the Buffalo Coulee crude responds better to alkaline fluid injection. This observation is statistically tested later in this section. The observation, however, is in harmony with the fact that the interfacial tensions measured for the Buffalo Coulee oil with various alkaline solutions were significantly lower than the corresponding W. Edam-alkaline solution systems.

Analysis of variance, similar to the W. Edam case, has also been carried out for the set of Buffalo Coulee alkaline flooding experiments. The ANOVA results are given in Tables 19 and 20, on the basis of the Buffalo Coulee oil recovery and water-oil ratios of Table 18. It is clear from the two tables that the calculated F-values for the main effects (feed rate, alkali types and alkali concentration) are not significant. The significance tests, therefore, confirm that there is no real difference between feed rate, alkali type or alkali concentration effects in the case of the Buffalo Coulee oil. This is unlike the West Edam oil runs, where the effect of concentration and feed rate proved to be significant. It appears that the high oil recovery results, of the Buffalo Coulee oil, have masked the differences between the main effects.

Because the W. Edam and Buffalo Coulee factorial sets of alkaline flooding experiments were carried out under identical conditions, with the type of oil as the only difference, it was possible to treat the two sets together as a 2^4 factorial experiment. Thus the analysis of variance was carried out by considering the combined set of sixteen alkaline displacement runs. In this case, the oil type was the fourth factor considered, in addition to feed rate, alkali type and concentration. Obviously each of these factors is considered at two levels; the two levels of oil are whether it is the Buffalo Coulee or W. Edam crude.

The analysis of variance calculations for the 2^4 factorial experiment are summarized in Table 21 and 22. The purpose of treating the data and carrying out the analysis in this way

TABLE 19

ALKALINE FLOODING 2³ FACTORIAL EXPERIMENT
SASKOIL BUFFALO COULEE CRUDE

ANALYSIS OF VARIANCE
(BASED ON OIL RECOVERY RESULTS)

Corrected Total Sum of Squares = 56.0
Degrees of Freedom = 7
Mean Square = 8.0

<u>Source of Variation</u>	<u>D.F.</u>	<u>S.S.</u>
Feed Rate	1	0.0
Additive Type	1	4.5
Additive Concentration	1	0.5
Rate x Type	1	0.5
Rate x Conc	1	0.5
Type x Conc	1	32.0
Rate x Type x Conc	1	18.0

Estimate of Error Variance = $(0.5 + 0.5 + 32.0 + 18.0)/4 = 12.75$

Test of Hypotheses Combining all ANOVA Interactions as an Error Term:

<u>Source</u>	<u>D.F.</u>	<u>S.S.</u>	<u>F Value</u>
Rate	1	0.0	0.0
Type	1	4.9	0.35
Conc	1	0.5	0.04

$F_{5\%}(1,4) = 7.71$, $F_{1\%}(1,4) = 21.2$

TABLE 20

ALKALINE FLOODING 2³ FACTORIAL EXPERIMENT
SASKOIL BUFFALO COULEE CRUDE

ANALYSIS OF VARIANCE
(BASED ON WATER-OIL RATIO RESULTS)

Corrected Total Sum of Squares = 0.979
Degrees of Freedom = 7
Mean Square = 0.14

<u>Source of Variation</u>	<u>D.F.</u>	<u>S.S.</u>
Feed Rate	1	0.001
Additive Type	1	0.101
Additive Concentration	1	0.031
Rate x Type	1	0.001
Rate x Conc	1	0.011
Type x Conc	1	0.551
Rate x Type x Conc	1	0.281

Estimate of Error Variance = $(0.001 + 0.011 + 0.551 + 0.281)/4$
= 0.211

Test of Hypotheses Combining all ANOVA Interactions as an
Error Term:

<u>Source</u>	<u>D.F.</u>	<u>S.S.</u>	<u>F Value</u>
Rate	1	0.001	0.005
Type	1	0.101	0.479
Conc	1	0.031	0.147

$F_{5\%}(1,4) = 7.71$, $F_{1\%}(1,4) = 21.2$

TABLE 21

ANOVA OF ALL SYNTHETIC CORE DISPLACEMENT EXPERIMENTS
(2⁴ FACTORIAL ANALYSIS BASED ON OIL RECOVERY)

Corrected Total Sum of Squares = 225.94
Degrees of Freedom = 15
Mean Square = 15.06

<u>Source of Variation</u>	<u>D.F.</u>	<u>S.S.</u>
Feed Rate	1	22.56
Additive Type	1	0.06
Additive Concentration	1	18.06
Oil	1	68.06
Rate x Type	1	3.06
Rate x Conc	1	0.06
Rate x Oil	1	22.56
Type x Oil	1	7.56
Type x Conc	1	10.56
Conc x Oil	1	27.56
Rate x Type x Conc x Oil	5	45.81

Test of Hypotheses using the ANOVA MS for Rate x Type x Conc x Oil as an error term:

<u>Source</u>	<u>D.F.</u>	<u>ANOVA S.S.</u>	<u>F. Value</u>	<u>PR>F</u>
Rate	1	22.56	2.46	0.1774
Type	1	0.06	0.01	0.9374
Conc	1	18.06	1.97	0.2193
Oil	1	68.06	7.43	0.0415

TABLE 22

ANOVA OF ALL SYNTHETIC CORE DISPLACEMENT EXPERIMENTS
(2⁴ FACTORIAL ANALYSIS BASED ON WATER-OIL RATIO)

Corrected Total Sum of Squares =
Degrees of Freedom =
Mean Square =

<u>Source of Variation</u>	<u>D.F.</u>	<u>S.S.</u>
Feed Rate	1	0.216
Additive Type	1	0.003
Additive Concentration	1	0.276
Oil	1	0.865
Rate x Type	1	0.001
Rate x Conc	1	0.000
Rate x Oil	1	0.265
Type x Oil	1	0.255
Type x Conc	1	0.116
Conc x Oil	1	0.601
Rate x Type x Conc x Oil	5	0.859

Test of Hypotheses using the ANOVA MS for Rate x Type x Conc
x Oil as an error term:

<u>Source</u>	<u>D.F.</u>	<u>ANOVA S.S.</u>	<u>F. Value</u>	<u>PR>F</u>
Rate	1	0.216	1.26	0.3129
Type	1	0.003	0.02	0.8996
Conc	1	0.276	1.60	0.2611
Oil	1	0.845	5.03	0.0749

was to formally test the statistical significance of the observed difference between the recovery results of the two oils. In addition, the relative significance of the main effects could be resolved over the entire combined set of data. The two tables show the standard ANOVA calculations for the main effects and the interactions. The F-values for the main effects have been calculated using the estimated ANOVA mean square for the feedrate x alkali type x alkali concentration x oil type as an error term. In the two tables, the significance probability (labeled PR) for each F-value, associated with each of the main effects, has been calculated to assess the relative significance of these effects. If this value is small, it indicates that the F is significant [49]. As can be seen in each of the two tables, 21 and 22, a very small value of PR has been calculated in the case of the oil effect. This indicates that the difference between the recovery of the two oils is significant. The effect of alkali concentration and injection rate follow with comparable PR values. The significance probability of the F-value associated with alkali type was very high, indicating very small difference between the effects of sodium hydroxide and sodium orthosilicate.

6. PRESERVED CORE DISPLACEMENT

To more closely approximate likely field behaviour, by including the influence of clays and studying the impact of possible formation damage, flooding of preserved reservoir cores was a necessary component of this project. Thus, comparative waterflooding and alkaline flooding experiments were carried out to investigate these effects, using only one of the alkaline mediums.

In all the preserved core displacements, plugs from a single W. Edam Sparky sand core (9C-24-48-21-W3M) were used. Moreover, only dry W. Edam oil (5-30-48) was employed. The injection fluids used in the study were brine, 0.1 g/L NaOH and 10 g/L NaOH in brine. As demonstrated, the performance of sodium hydroxide and sodium orthosilicate shows very similar IFT characteristics and synthetic core displacements. However, since the chemistry of the preserved core and formation water interactions will be different for the two alkaline media studied, a complete evaluation of their relative merits would also require preserved core displacement studies with sodium orthosilicate. In this present contract, time did not permit this additional study.

6.1 Preserved Core Displacement Procedure

Core plugs of cylindrical shape were cut in a direction perpendicular to the main axis of a W. Edam Sparky core. The original W. Edam core was carefully preserved in dry ice during transportation, and stored in a freezer after it was received at Gulf R&D. Handling of sections of the core, during plug preparation, was minimized and cooling with dry ice was always used during necessary handling.

The following procedure was consistently used in each of the displacement experiments:

- . The core plug was mounted in a teflon sleeve into a Hassler-type core holder, as shown in Figure 24. All core plugs used in this set of experiments were 2.5 cm in diameter, and varied in length between 12.1 and 13.8 cm.
- . The mounted plug was left to thaw for at least 24 hours under a confining pressure of 1000-1100 psig. The confining pressure was maintained throughout each experiment, until all measurements were completed and samples were collected.

Hassler flow cell

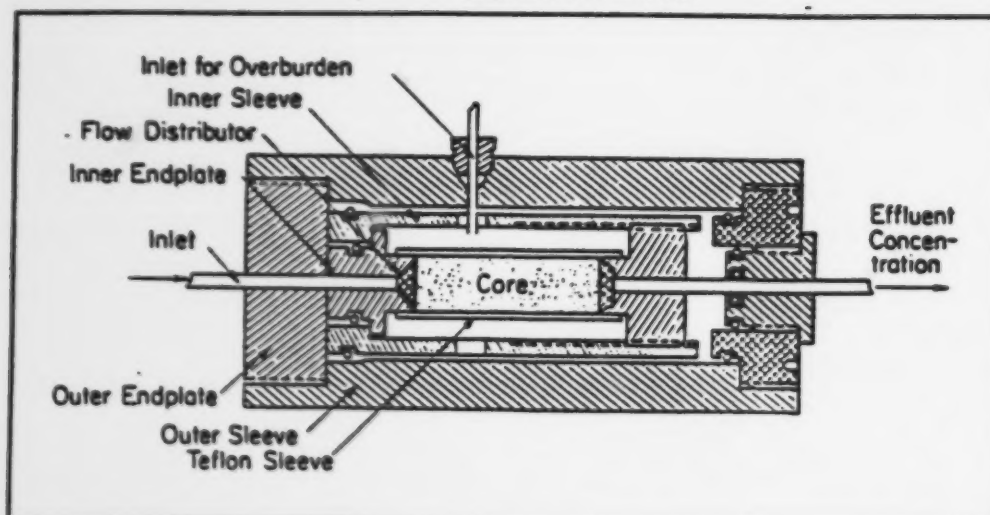


FIGURE 24

HASSLER-TYPE CORE HOLDER FOR
PRESERVED CORE DISPLACEMENT

- . To standardize the initial conditions, and to be able to make meaningful comparisons between different runs, the core plug was flushed with toluene followed by pentane until it was completely cleaned of the original reservoir fluids. The core plug was then dried with nitrogen.
- . The dry core plug was saturated with brine, which was allowed to flow through for several hours. After ensuring complete saturation, as indicated by the absence of air bubbles and the constancy of pressure drop at a specific flow rate, the pore volume was determined through a mass balance on brine injected and produced.
- . Accurate flow measurements were also taken. At steady-state conditions, a brine sample was collected, over a recorded period of time, and weighed. The pressure drop across the core plug was, simultaneously, measured using a transducer-recorder arrangement. Knowing the viscosity of brine and dimensions of the core plug, the absolute permeability was calculated according to Darcy's law. Flow measurements were repeated and the average permeability was calculated. Care was taken to consider only permeability values within Darcy's flow regime, i.e. linear pressure drop-flow rate relationship.
- . West Edam oil (5-30-48) was then injected to drive the core plug to connate water saturation. The fraction of pore volume occupied by oil (HCPV) was obtained by determining the amount of water driven out of the core plug using the Dean-Stark method. The level of connate water saturation is the difference between PV and HCPV. After equilibrium, the effective permeability to oil was sometimes measured to verify the permeability to brine, particularly if the pressure drop to the latter was unreliably low.
- . The displacement of oil was then started using the appropriate injection fluid (brine or sodium hydroxide in brine) at a constant rate.

- . The displaced product was collected, at short time intervals at the beginning of a run and at longer intervals later in the run, and analyzed for water-oil content.
- . The run was terminated after injecting about 7 pore volumes of fluid.

Analysis of produced samples was carried out using a spectrophotometric method, which has been recently developed and tested at Gulf R&D, for the determination of oil and water content [50]. In this method the oil and water in the sample are dissolved in tetrahydrofuran, with subsequent determination of the oil using visible spectrophotometry and water using infrared spectrophotometry. The method was particularly suited for the small volume of samples collected; whereas other standard methods, such as Dean-Stark, could have been unreliable. In view of the large number of samples analyzed, the speed of the method was an added convenience.

Five preserved core displacement runs were carried out following the procedure described above. The injection fluids used in the experiments were as follows:

- . Run PC1 : the displacing fluid was brine solution.
- . Run PC2 : alkaline solution of NaOH in brine, containing a trace of sodium hydroxide to give a pH of 8.57.
- . Run PC3 : 10 g/L NaOH solution in brine.
- . Run PC4 : 0.1 g/L NaOH solution in brine.
- . Run PC5 : brine solution was initially used as the injection fluid. After injecting about 6 PV of brine, to nearly reach the irreducible oil saturation, the run was continued by injecting another 6 PV of 0.1 g/L NaOH in brine.

Low permeability core plugs were used in Runs PC1 to PC3; whereas higher permeability plugs were employed in Runs PC4 and PC5.

6.2 Preserved Core Displacement Results and Discussion

The complete results of the preserved core displacement runs are given in Appendix B, Tables B1 to B5. Each table lists the amount of produced fluid sample (which is equal to the amount of injected fluid under steady-state conditions), percent oil and percent water in each sample. Also included in the tables are the calculated cumulative amount of oil and cumulative amount of water, after normalizing the oil and water content of each sample. In the spectrophotometric method of analyzing the produced fluid sample, both the oil and water content are determined independent of each other, rather than determining one and calculating the other by difference as in Dean-Stark's method. For this reason, however, the % oil and % water in Tables B1 to B5 do not always add to exactly one hundred. To correct for this, all sums of % oil and % water were normalized to 100, and the oil and water content in each sample was accordingly calculated. In each of Appendix B tables, the values determined for permeability, porosity, pore volume and hydrocarbon pore volume, of each of the core plugs, are also included.

Figures 25 and 26 illustrate the cumulative oil recovery and water-oil ratio results obtained with the lower permeability core plugs. Figures 27 and 28 show the corresponding higher permeability core plug run results. Figure 25 demonstrates a significant increase in oil recovery as a result of injecting the 10 g/L NaOH solution. The increase amounts to over 0.1 HCPV, or 30% over the amount of oil recovered by brine injection. Even the injection of only a slightly alkaline NaOH solution (pH 8.57), Run PC2, amounted to nearly as high an improvement in oil recovery. Oil is recovered at a much faster rate, however, in the case of the 10 g/L NaOH solution. Figure 26 exhibits the recovery results in terms of the cumulative water-oil ratio. Consistent with Figure 25, the highest water-oil ratios are those corresponding to the brine run, while the lowest are those of the 10 g/L NaOH run PC3.

The first three plugs, used in Runs PC1 to PC3, were cut from the same core as those used in Runs PC4 and PC5. However, there was considerable difference in their characteristics.

FIGURE 25
CUMULATIVE OIL RECOVERY, LOW PERMEABILITY W. EDAM

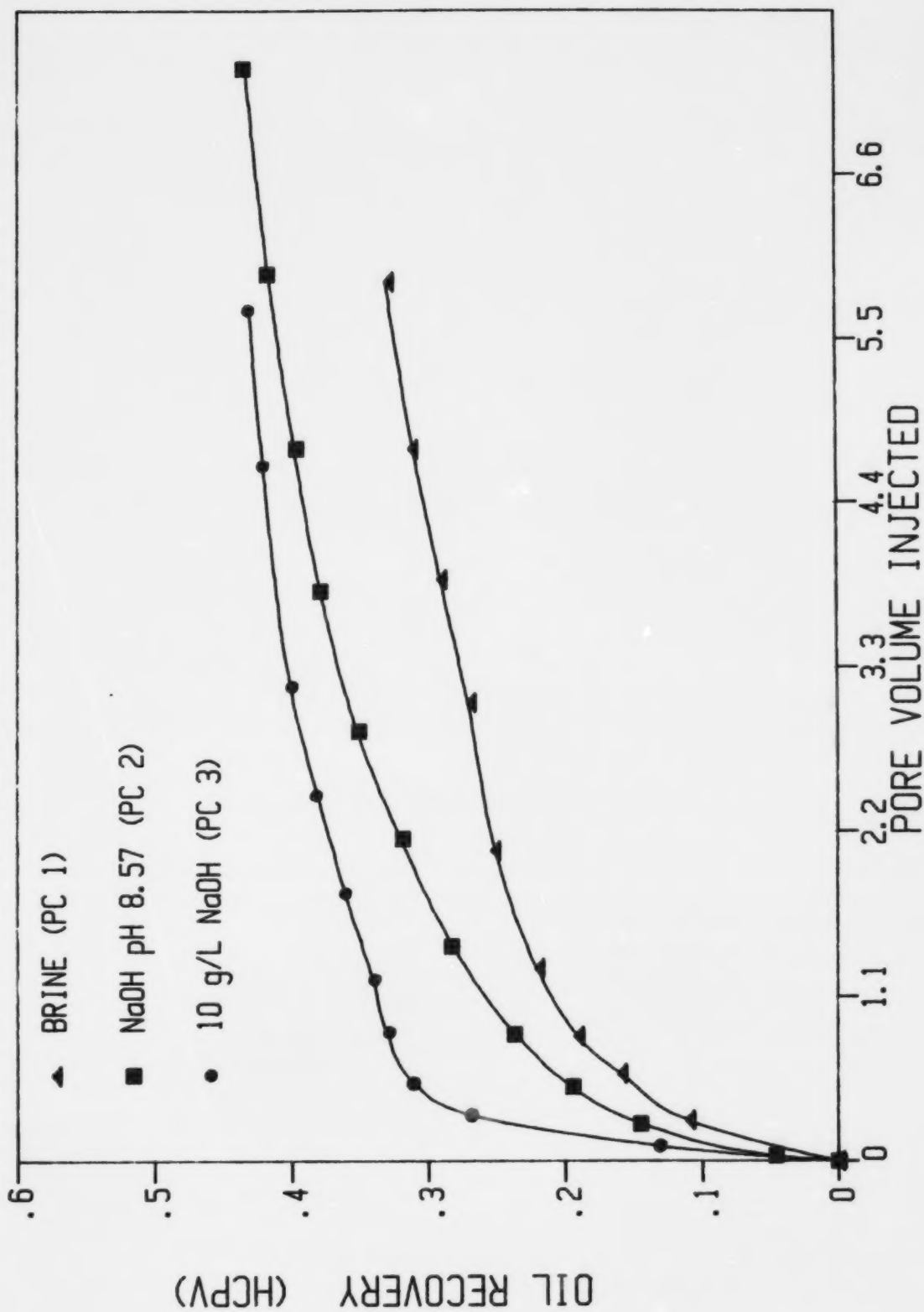


FIGURE 26

CUMULATIVE WATER-OIL RATIO, LOW PERMEABILITY W. EDAM

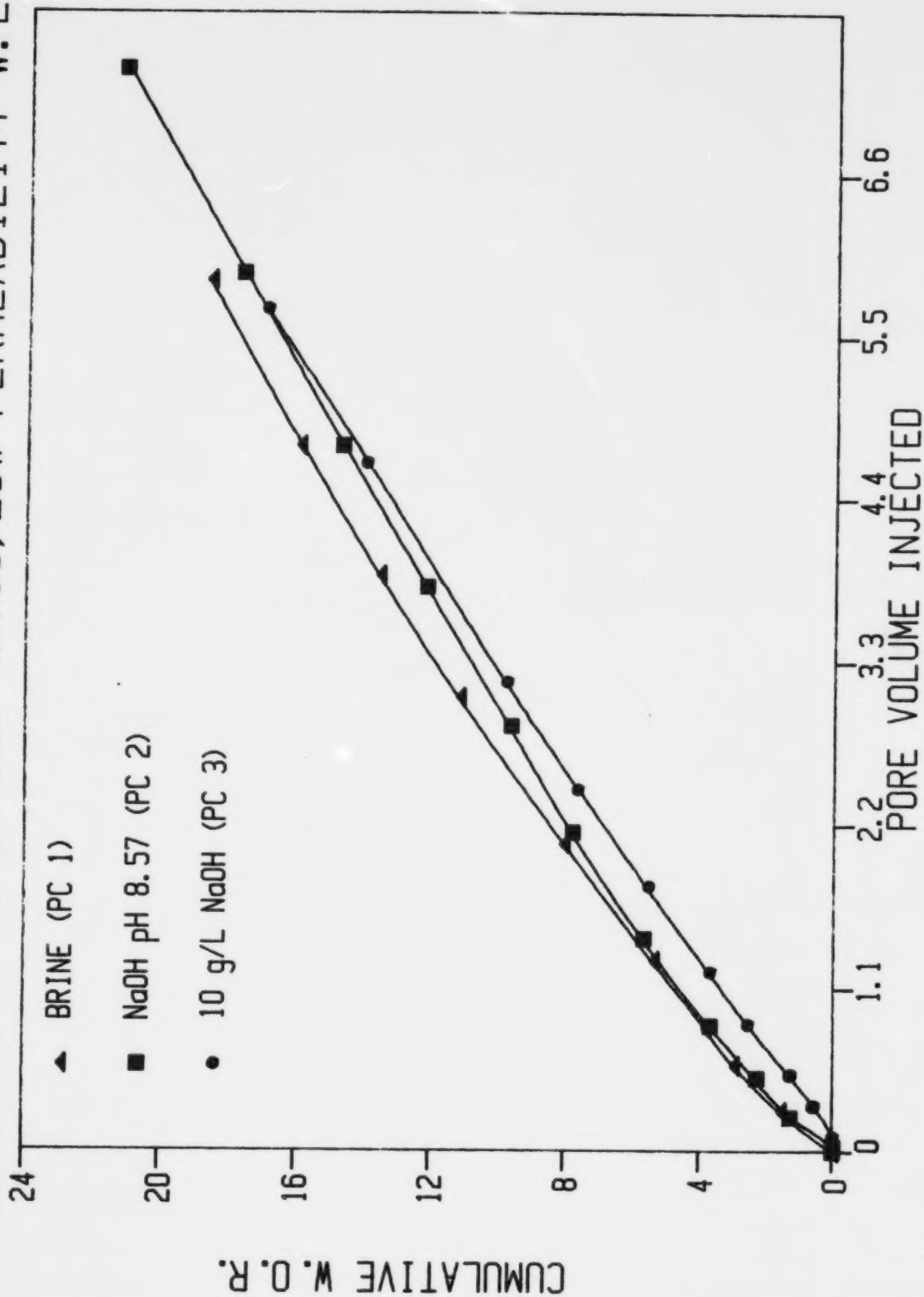


FIGURE 27

CUMULATIVE OIL RECOVERY, HIGH PERMEABILITY W. EDAM

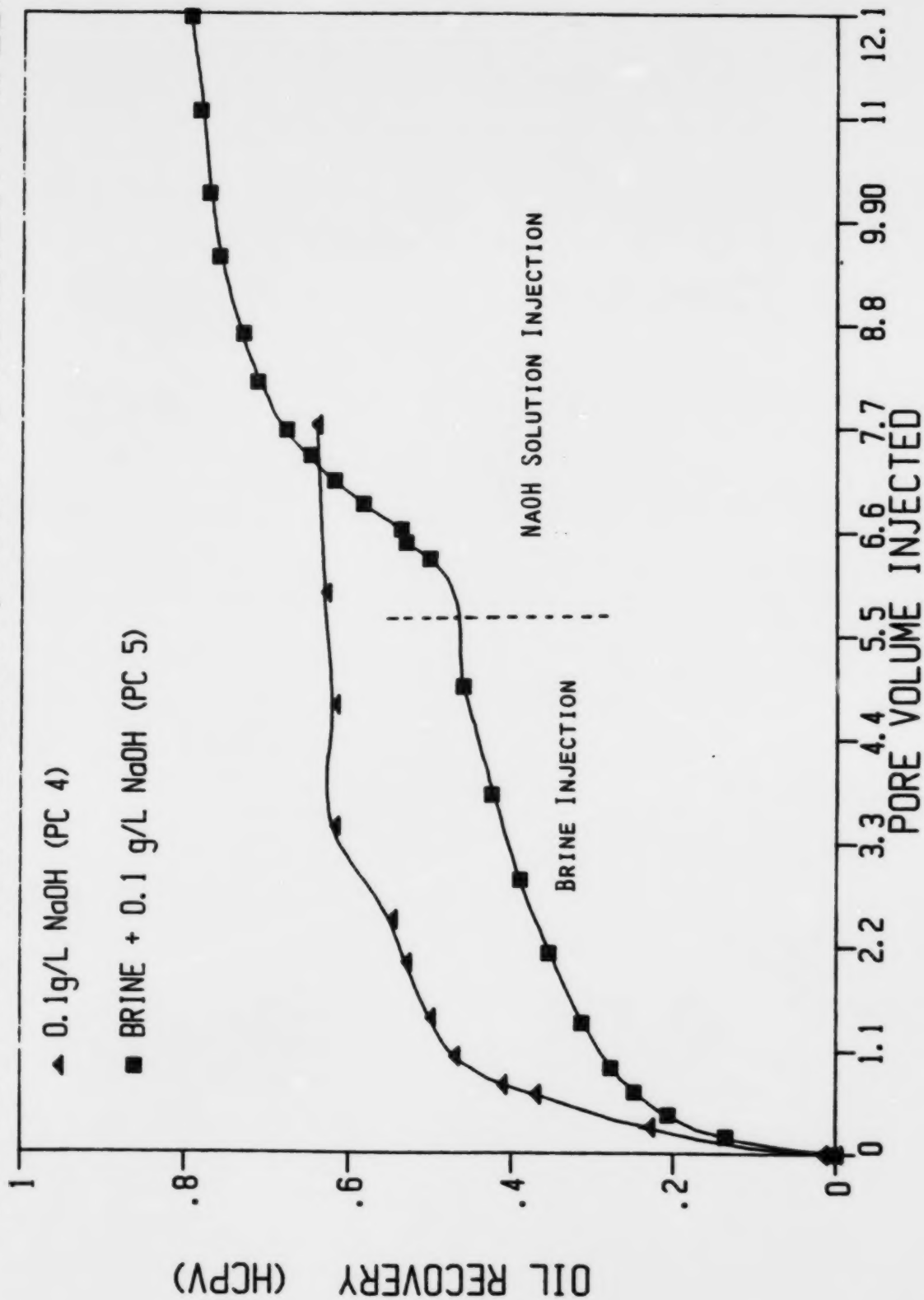
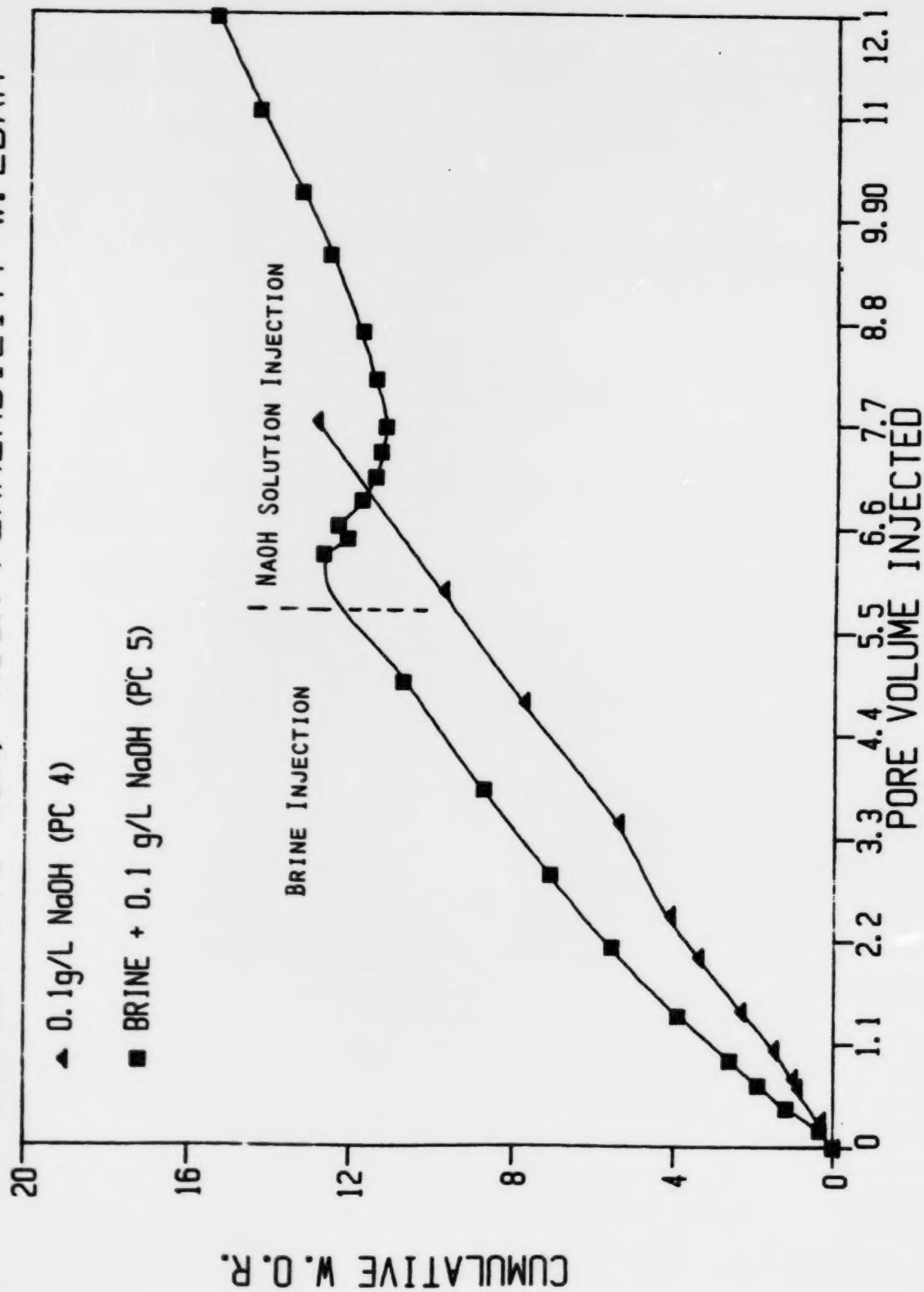


FIGURE 28
CUMULATIVE WOR, HIGH PERMEABILITY W. EDAM



In particular the permeability of the first three plugs were considerably lower than those of the plugs used in Runs PC4 and PC5, as can be seen by comparing the results of Tables B1 to B3 with Tables B4 and B5. Moreover, the connate water saturations in the first set of experiments, especially in Runs PC2 and PC3, were significantly higher than those in the second set (Runs PC4 and PC5). In Runs PC2 and PC3, the connate water saturations in the core plugs were over 0.20 PV, while in Runs PC4 and PC5 the connate water saturations were around 0.1 PV. The observed differences indicate that the section of the core used for the first three plugs had possibly higher clay content than the section used for the following set of plugs. Varying clay content in sections of the same core is a common occurrence in cores obtained from many Saskatchewan and Alberta reservoirs. There is finally one additional factor, which may not be as important, but might have had some influence on the characteristics of the two sets of plugs. The technique of cutting and mounting the plugs in teflon sleeves was varied slightly after Run PC3.

Comparison of Figure 25 with 27 shows that brine injection in the initial part of Run PC5 results in higher recovery than brine injection in Run PC1. This is consistent with the observed differences in the two sets of core plugs. At about 6 PV of brine injection, the WOR in Run PC5 is about 13 as compared with 19 in Run PC1.

Figures 27 and 28 display the effect of 0.1 g/L NaOH solution injection on the recovery behaviour, in comparison with brine only injection. Run PC4 shows that 0.1 g/L NaOH injection results in a much higher recovery than the comparable brine injection part of Run PC5. The relative increase in oil recovery is even higher than that obtained with 10 g/L NaOH in the previous set of experiments, PC3 compared with PC1.

Run PC5 was designed to test the effect of alkaline fluid injection after brine displaces the oil down to nearly the irreducible level. The results show that nearly 0.3 HCPV of additional oil was recovered due to the injection of 0.1 g/L NaOH solution. An abrupt drop in water-oil ratio, which eventually increases once again, accompanies the alkaline

fluid injection. The oil recovery curve also shows the highest ultimate recovery obtained in any of the runs. Run PC4, on the other hand, shows lower ultimate oil recovery than PC5, but much faster rate of recovery. Because the latter effect is the overriding factor in most applications, it is probably better to start with alkali solution injection at the inception of an alkaline flooding project.

7. EMULSION STUDY

It has already been stated that emulsification is believed to be a major mechanism of oil recovery by alkali solution injection, especially with heavy oils. Because of their higher asphaltene and porphyrin content, heavy oils can emulsify, with alkaline water, much more readily than light oils. There is disagreement, however, as to the type of emulsions formed (i.e. water-in-oil or oil-in-water), and to the exact role of the formed emulsions in recovering additional oil.

For the sake of completeness of this study it was felt necessary to examine the basic emulsification characteristics of the oils/alkaline solutions considered in this project. Standard emulsion tests, similar to those suggested in the API RP42 procedure, were followed. Microscopic-photographic recording of samples of the formed emulsions was also used. Moreover, few produced fluid samples, from the 0.1 g/L NaOH preserved core displacement run PC4, were also examined.

The standard emulsification tests were designed to indicate the tendency of W. Edam oil (5-30-48)-brine system and Buffalo Coulee oil-brine system to emulsify due to the presence of an alkaline additive. The following five mixtures were examined for each of the two oils:

1. Oil/brine.
2. Oil/0.1 g/L NaOH in brine.
3. Oil/10 g/L NaOH in brine.
4. Oil/0.1 g/L METSO 200 in brine.
5. Oil/10 g/L METSO 200 in brine.

7.1 Emulsion Preparation

Following the API RP42 procedure, the equipment and materials for emulsion testing included:

- (a) High speed stirrer (mixer) [Hamilton Beach Model 936 with standard disc head].

- (b) 400 mL tall form beakers for mixing, 100 mL graduated cylinders, timers, and graduated syringes.
- (c) Crude oil (both W. Edam and Buffalo Coulee oils).
- (d) Alkaline solutions (NaOH and METSO 200 as indicated above).

The API procedure calls for the presence of finely divided solids (silica or core material) to enhance the stability of the emulsions. We have not found it necessary to add any solid particles; for emulsions formed readily in the presence of the alkaline additives. Moreover, adding the solids would have complicated the interpretation of the results.

The following steps were consistently used for emulsion preparation:

- 50 mL of crude oil were added to 50 mL of each of the brine and alkaline brine solutions
 - the mixture was emulsified with the stirrer at 16000 rpm for 30 seconds
 - the emulsion was poured immediately into a 100 mL graduated cylinder
 - volume of water breakout was recorded with time
 - samples from the oil phase and water phase were taken with the syringe at several time intervals. No attempt was made to take samples from the thick emulsion water-oil interface zone
 - the samples were photographed at different magnifications (10, 20 or 40 X) using a Nikon microscope arrangement.
- All Figs. 29-36 have an actual magnification of 200:1.

7.2 Emulsions Observations

Mainly qualitative data has been obtained from the emulsion study. The study, however, was very useful in verifying and explaining some of the earlier results and alkaline additive effects. The observations derived from the above outlined experiments are given in the following, and are illustrated with representative photomicrographs:

- . Very little emulsification was observed for the brine mixture with either of the two oils. Thus, nearly complete breakout of the oil and water phases was observed

only one minute after the mixture was left to settle. Microscopic examination of oil-phase samples showed negligible water-in-oil droplets.

- . The oil-brine mixture readily emulsified in the presence of either of the two alkalies (NaOH or METSO 200) at each of the two concentrations (0.1 or 10 g/L). The emulsions were stable for several hours. Only after 1 to 3 days did significant breakout of the oil and water phases take place.
- . The two alkaline additives, at the same concentration and with each of the two oils, behaved very similarly to each other. The emulsions formed in the case of the W. Edam oil are exemplified in Figures 29 and 30. This observation supports earlier IFT and displacement results; where it was found that the alkali type had little effect on the results.
- . Comparing Figure 29 with Figure 30, on the other hand, shows more pronounced additive concentration effect, particularly in the case of NaOH. Thus, the 10 g/L alkali solutions (NaOH or METSO) showed generally tighter water-in-oil emulsions, than the 0.1 g/L solutions, and were characterized by a wider size distribution of the water droplets in oil. This was also demonstrated by a slower breakout of the water phase from the oil phase in the case of the 10 g/L alkaline solution. This additive concentration effect was particularly clear in the case of W. Edam oil. On the other hand, the Buffalo Coulee oil/0.1 and 10 g/L NaOH emulsions had similar breakout behaviour. The photomicrographs, Figures 31 and 32, also reflect this observation. This little difference in emulsification characteristics may explain the relatively insignificant effect of additive concentration on the Saskoil crude displacement results.
- . Samples taken from the water phase revealed the presence of oil-in-water emulsions in every case. Figures 33 and 34 show examples of the oil-in-water emulsions observed for the W. Edam oil with the four different alkaline solutions. This demonstrated that the emulsification and

entrainment mechanism must have contributed to the enhancement of oil recovery in the displacement experiments.

- . It has already been mentioned that a tighter more stable water-in-oil emulsion was observed in the case of the 10 g/L alkali in brine (NaOH or METSO with each of the two oils). Interestingly, however, it was observed that the water phase remained brownish in colour in the case of the 0.1 g/L alkali, even after several days, while it was very clear in the case of the 10 g/L alkali. This suggested a higher degree of oil-in-water emulsification in the former case. It also points to a more significant contribution to oil recovery by the mechanism of emulsification and entrainment in the case of 0.1 g/L alkaline concentration. The photomicrographs, Figure 35, support this observation. It is interesting to note in the figure that the 0.1 g/L METSO case exhibits a higher degree of oil-in-water emulsion than the 10 g/L case, even though the former picture was taken three hours after emulsification. The 10 g/L METSO picture used a sample freshly taken from the water phase.
- . We finally illustrate the presence of emulsions in the produced sample from one of the preserved core displacement runs, Run PC4. Figure 36 displays photomicrographs of produced fluid samples taken after 0.5 PV and 7.5 PV injection respectively. The emulsions demonstrate similar characteristics as observed in the mixing experiments. It is interesting to note that the emulsification persists even after 7.5 PV of fluid injection.

ALL PHOTOMICROGRAPHS IN FIGURES 29-36 HAVE AN ACTUAL MAGNIFICATION OF 200:1.



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FIGURE 30

OIL PHASE EMULSION
(W. EDAM OIL - 10 G/L ALKALI)

W. EDAM - 10 G/L NAOH

W. EDAM - 10 G/L METSO



FIGURE 31

EFFECT OF NAOH CONCENTRATION ON
BUFFALO COULEE OIL PHASE EMULSIONS

BUFFALO COULEE - 0.1 G/L NAOH

BUFFALO COULEE - 10 G/L NAOH

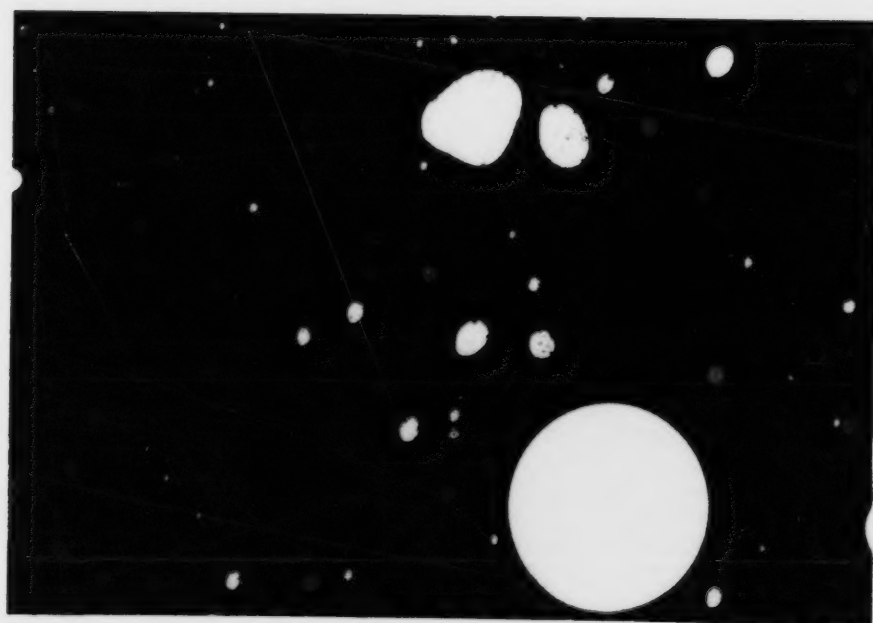
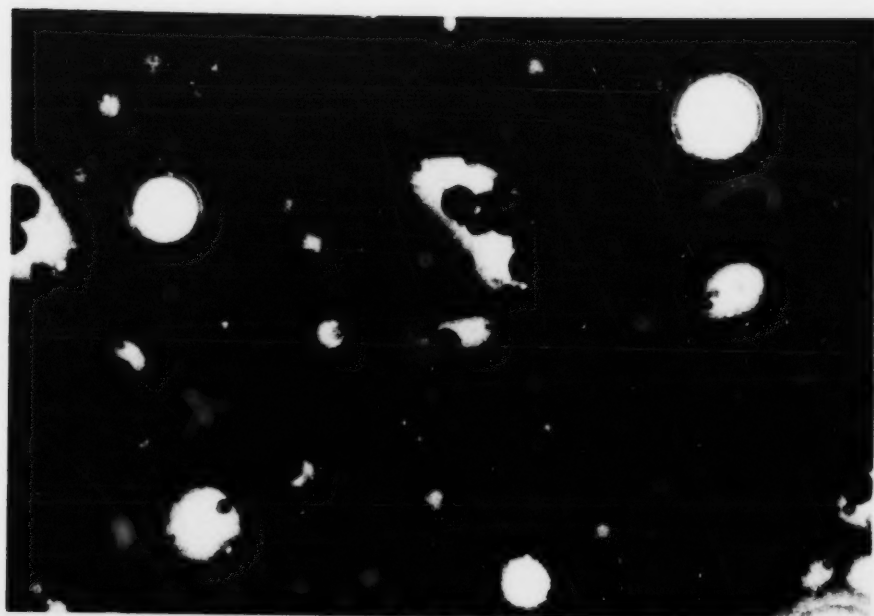


FIGURE 32

EFFECT OF METSO 200 CONCENTRATION ON
BUFFALO COULEE OIL PHASE EMULSIONS

BUFFALO COULEE - 0.1 G/L METSO

BUFFALO COULEE - 10 G/L METSO

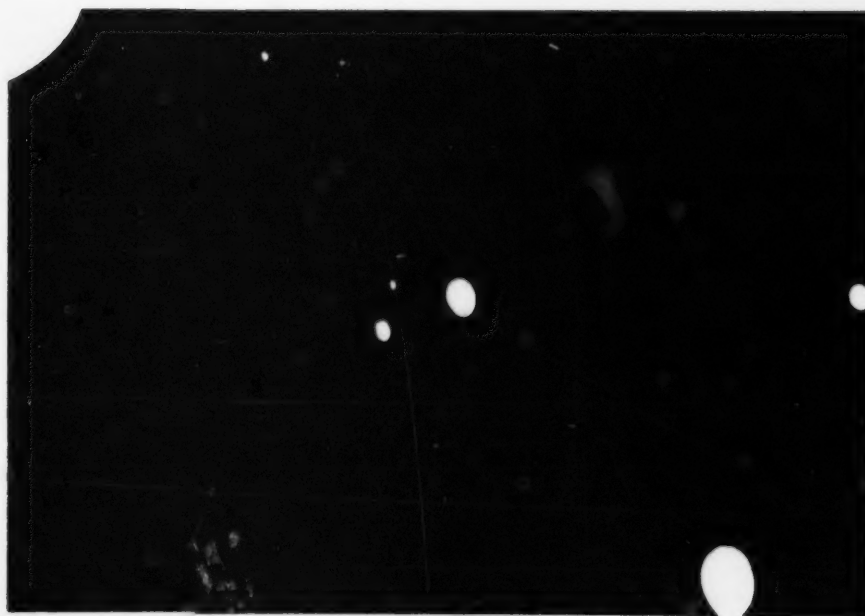
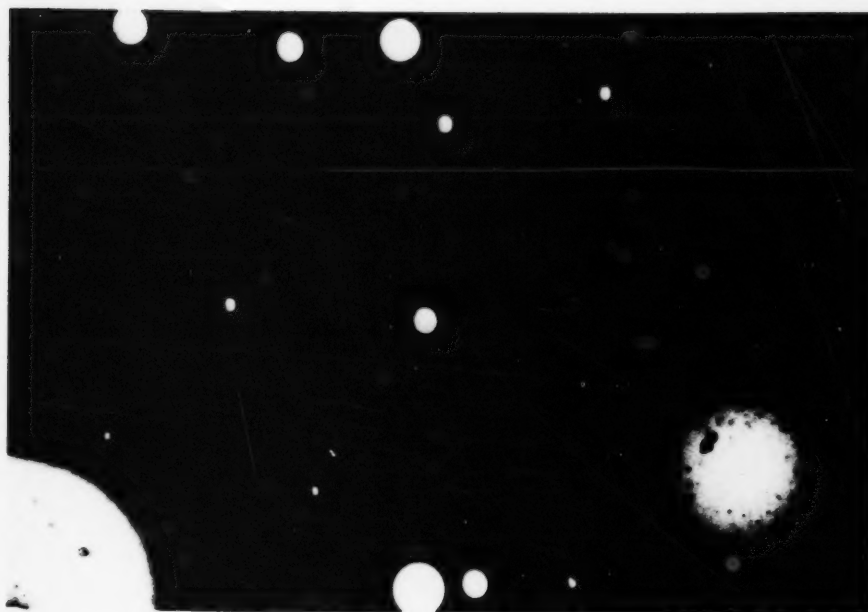


FIGURE 33

EFFECT OF NAOH CONCENTRATION ON
W. EDAM WATER PHASE EMULSIONS

W. EDAM - 0.1 G/L NAOH

W. EDAM - 10 G/L NAOH

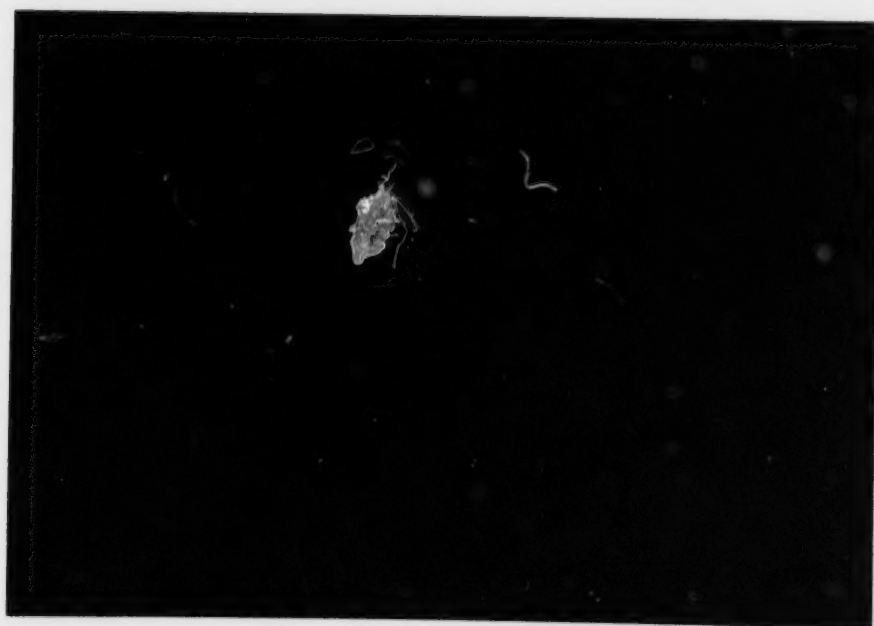
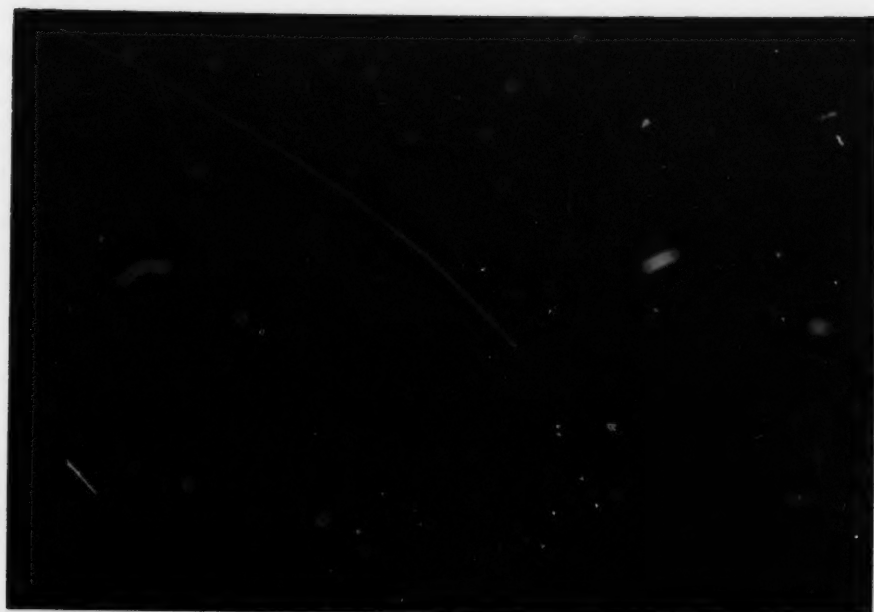


FIGURE 34

EFFECT OF METSO 200 CONCENTRATION ON
W. EDAM WATER PHASE EMULSIONS

W. EDAM - 0.1 G/L METSO

W. EDAM - 10 G/L METSO



FIGURE 35

EFFECT OF METSO 200 CONCENTRATION ON
BUFFALO COULEE WATER PHASE EMULSIONS

BUFFALO COULEE - 0.1 G/L METSO

BUFFALO COULEE - 10 G/L METSO

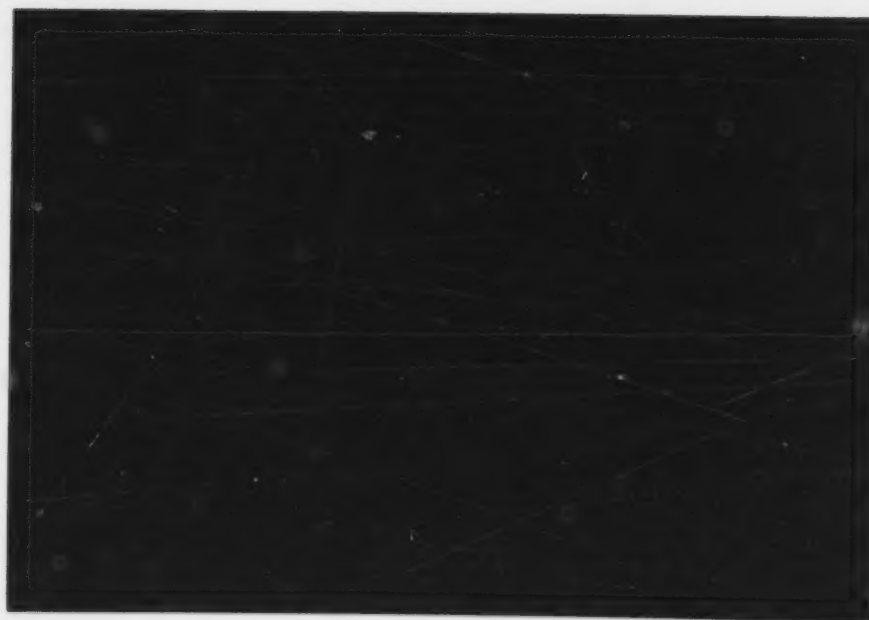
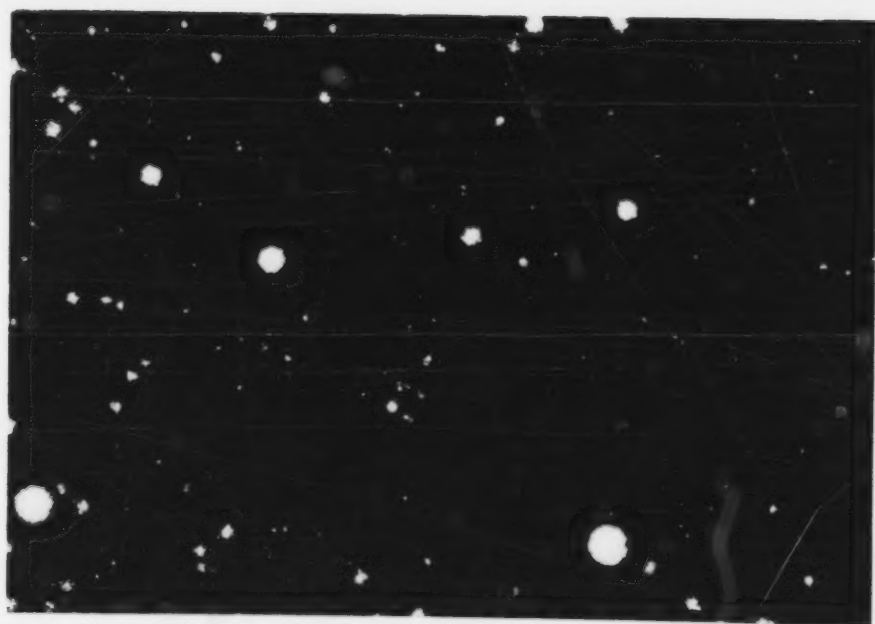
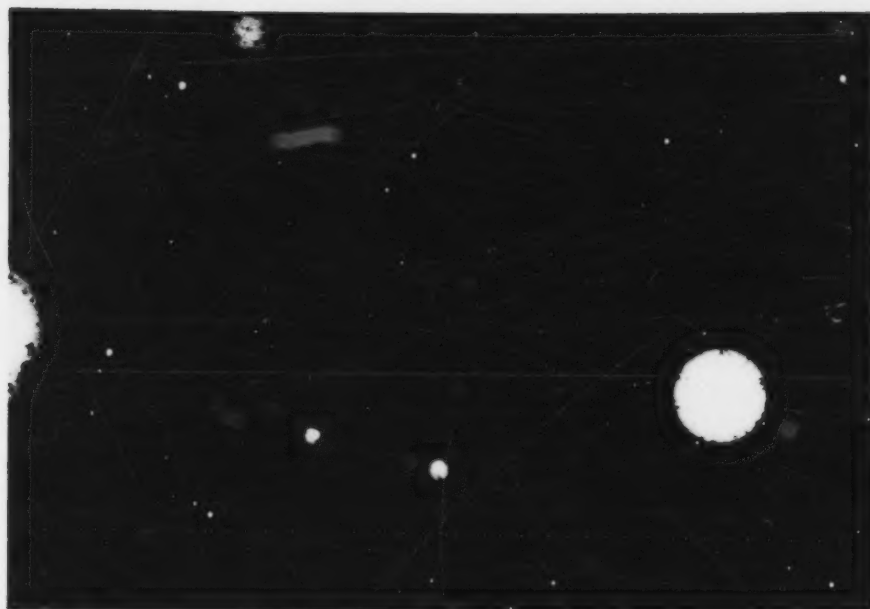


FIGURE 36

PRODUCED FLUID EMULSIONS IN
PRESERVED CORE DISPLACEMENT RUN PC4

PRODUCED FLUID EMULSION
AT 0.5 PV FLUID INJECTION

PRODUCED FLUID EMULSION
AT 7.5 PV FLUID INJECTION



8. ROCK REACTIVITY

8.1 Introduction

The maintenance of an effective level of alkalinity during an alkaline flood is of prime importance to the success of the project [5, 52]. Certain types of minerals, for example gypsum, dolomite and clays, can have a significant effect on caustic consumption due to ion exchange, chemical reactions and precipitation. These reactions can also lead to the formation of new minerals (e.g. scale) and reduced permeability. The loss of alkalinity varies significantly from reservoir to reservoir due to differences in mineralogy, formation water composition, flood chemical composition and concentration, and reservoir conditions, such as temperature [53-56]. The magnitude of alkalinity loss, rate of loss and the causes should be known in order to effectively design a flood.

This task determines reactivity of an Edam core, well 9C-24-48-21-W3M, under static conditions with (i) brine 2.0 g Na/L; (ii) sodium hydroxide in brine at concentrations of 0.1 g/L and 10 g NaOH/L; and (iii) Metso 200 in brine at concentrations of 0.1 g/L and 10 g Metso/L.

Sodium, silicon and trace elements were analyzed on all starting solutions and leachates to determine ion exchange, chemical reaction and depletion of flood chemicals. In addition the caustic consumption was determined over a wide pH range.

8.2 Experimental

8.2.1 Core Preparation

A section of core was cut from Edam well 9C-24-48-21-W3M at a depth of 461.2 m. Two batches of approximately 700 g were mounted in glass tubes and extracted at 23°C with toluene until no bitumen was evident in the effluent. Pentane was then pumped through the core materials to remove the toluene and the cores were then dried at 23°C. Each extracted batch

of core was sieved to determine if a large percentage of fine material was present (Table 34). All fractions from both batches were then recombined and homogenized.

Brine containing 2.0 g Na/L was added to the total blend to saturate the pore space and just cover the sand. This brine was left in contact with the core for two days to condition the core and remove any salts that might have precipitated from the formation water (Table 5) during the solvent extraction. The brine was drained from the core material using a 8 μ m millipore filter. The core was divided into six equal parts, including one retain sample (F1) and the five parts used in the rock reactivity study (F2-F6).

8.2.2 Rock Reactivity Study

Polyethylene containers with "O" ring seals were washed with dilute hydrochloric acid followed by several rinses with distilled water and a prolonged soak in distilled water.

Equal amounts of core material were weighed into the bottles and the following solutions added:

- F2 - Core + Brine containing 2.0 g Na/L.
- F3 - Core + 0.1 g NaOH/L in brine
- F4 - Core + 10 g NaOH/L in brine
- F5 - Core + 0.1 g Metso 200/L in brine
- F6 - Core + 10 g Metso 200/L in brine

Enough aqueous solution was added to just cover the core material. This resulted in a ratio of core to aqueous solution of approximately 5:1. The bottles were flushed with nitrogen and tightly capped. The core samples were in contact with the liquids for 36 days with shaking for 8 hours/working day. (The original aqueous solutions were also stored in cleaned polyethylene bottles for 36 days.)

After 36 days the liquid from each sample was decanted, centrifuged for 8 minutes at 20 000 RPM and then filtered through a 0.45 μ m disposable millipore filter assembly (no glass) using disposable plastic syringes. The liquid from each sample was split into two portions, for caustic consumption analysis and for elemental analysis.

8.2.3 Analysis

Multielement

Aliquots (1.5 g) were weighed into 5 mL volumetric flasks. Hydrochloric acid (1.5 mL) was added to each sample and the resulting solutions were diluted to volume for analysis by DC plasma emission spectrophotometry. Quantitation was by method of standard additions. Lithium nitrate (2000 mg/L) was added to the samples and standards as an ionization buffer.

Silicon

The original samples were diluted with deionized water (no acid) for analysis by DC plasma emission spectrophotometry. Quantitation was by the method of standard additions.

Sodium

The original samples were diluted with deionized water (no acid) for analysis by flame atomic absorption spectrophotometry at 330.2 nm. Cesium (1000 mg/L) was added to the samples and standards as an ionization buffer. This method generally promotes better precision and accuracy for sodium at high concentrations than the plasma analysis.

Alkali Consumption

The original solutions and the leachate solutions were titrated with 0.005 N HCl or 0.5 N HCl (10 g/L of NaOH or Metso 200 samples). The pH values were recorded over the entire range from pH 13 to 3. The choice of pH to use as an end point can vary with the crude [55], reservoir conditions and buffering of the solutions [8]. In this study, pH values of 10.5 (based on IFT data), 8.3 (hydroxide end point) and 7.6 (pH of reservoir water - Table 5) were used for caustic consumption calculations.

Buffering of silicate solutions is well documented [8,59,60]. Silicate species in solution $\text{Si}_2(\text{OH})_3\text{O}^-$, $\text{Si}(\text{OH})_2\text{O}_2^-$, $\text{Si}(\text{OH})\text{O}_3^-$, etc., are stable at high pH and convert to nonionic species $\text{Si}(\text{OH})_4$ at pH 9 or lower. As a result, the concentration of OH^- ions in such buffered solutions depends upon the specified pH [8, 55]. Titration curves for all original solutions and leachates have been included to enable accurate assessment of the alkali consumption.

Alkalinity consumption in meq/100 g core at a given pH in this work is defined as

$$= \frac{100 \text{ NL}(V_1 - V_2)}{W_C A}$$

where N = normality of titrant
L = weight of liquid used in leach
W_C = weight of core used in leach
A = weight of aliquot titrated
V₁ = mL of titrant required for original solution
V₂ = mL of titrant required for leachate

and % alkali consumption at a given pH

$$= \left(\frac{V_1 - V_2}{V_1} \right) \times 100\%.$$

8.3 Results and Discussion

8.3.1 Conditioning of Core With Brine - Two Days

The core material (Section 8.2.1) was conditioned for two days in the flood brine in order to (i) remove any salts that may have precipitated from the formation water during removal of the bitumen and subsequent drying, and (ii) simulate a brine preflush in the field. A sample of formation water from Edam contained approximately 20 600 mg Na/L, 427 mg K/L, 680 mg Ca/L and 730 mg Mg/L (Table 5), whereas the flood water contained an order of magnitude less sodium and no other metals.

The composition of the brine drained from the core after two days is shown in Table 23. (The solid/brine ratio of approximately 5:1 was selected in order that the brine just filled the pore spaces.) Sodium, calcium, magnesium and potassium concentrations increased by 850 mg Na/kg, 40 mg Ca/kg, 15 mg Mg/kg and 30 mg K/kg. Silicon and boron concentrations increased slightly.

8.3.2 Brine Leach - 36 Days

Several elements increased in concentration in the brine during the 36 day leach as shown in Table 24. The most significant increases were for calcium 100 mg/kg, magnesium 25.6 mg/kg, potassium 30.1 mg/kg and silicon 8.3 mg/kg.

During the leach the brine dissolved some buffering agents (pH 6-7) as shown by the titration Table 27 and Figure 37.

8.3.3 Sodium Hydroxide Leaches

The F3 leachate (with 0.1 g NaOH/L) was almost identical in elemental composition to the brine leachate, except that the magnesium concentration decreased from 25.6 mg/L for brine to 8.14 mg/L, probably due to the low solubility of magnesium hydroxide in caustic solutions (Tables 24 and 25).

The titration curve for the F3 leachate was very similar to that of the brine (Tables 27 and 28 and Figures 37 and 38). The pH of the 0.1 g NaOH/L solution dropped from 10.40 to 7.95 during the leach and very little, if any, effective alkalinity remained (Tables 30 and 31).

The F4 leach (10 g NaOH/L) resulted in a large decrease (2200 mg Na/kg) in sodium concentration from 7620 to 5400 mg/kg (Table 25). Calcium and magnesium values were low at <1 mg/kg. As the pH increases, the solubility of Ca(OH)_2 decreases until, in strong caustic solution, it is insoluble [57]. Silicon, aluminum and boron concentrations increased as expected in strong alkali solutions to 172, 74 and 1.32 mg/kg respectively.

A large decrease in alkalinity occurred during the leach; with the pH dropping from 12.71 to 12.20. The titration curves for the original 10 g NaOH/L and the leachate are shown in Table 28 and Figure 39. The F4 leachate solution was buffered in comparison to the original NaOH solution due to dissolution of core material. Thus, alkali consumption is best estimated from the titration curves than from one specific pH value. The alkali consumption was significant at 3.57 to 4.01 meg/100 g core and corresponds to a 69.5% alkalinity loss at pH 10.5 (Tables 30 and 31).

8.3.4 Metso 200 Leaches

The F5 leachate was similar in composition to that of the brine and dilute (0.1 g NaOH/L) sodium hydroxide solution. There was a slight decrease in the silicon concentration from the original Metso 200 solution. The hardness ions were not significantly removed from solution at this concentration of orthosilicate (Table 26).

The titration curve for the F5 leachate again was similar to that of the brine (Tables 27 and 29 and Figures 37 and 40). The pH of 0.1 g Metso 200/L dropped from 10.54 to 7.54 during the leach. It is doubtful that any effective alkalinity remains at this pH (Tables 29, 30 and 31).

The F6 leachate (10 g Metso 200/L) showed dramatic decreases in both sodium and silicon concentrations from 6480 to 3980 mg/kg for sodium and 1260 to 514 mg/kg for silicon (Table 26). Thus, approximately 56-59% of the Metso 200 was precipitated from solution. When this large a quantity of material, roughly 5600-5900 mg/kg, is removed from solution by the formation of new minerals, the impact on reservoir permeability should be assessed.

The shape of the unreacted Metso 200 (10 g/L) titration curve is very different from that of 10 g/L NaOH due to buffering from the silicate species (Figures 39 and 41).

A large decrease in alkalinity occurred during the F6 leach and the pH dropped from 12.34 to 11.64 (Table 29). At pH 10.5 the alkali consumption was 2.38 mg/100 g core, or 74% (Tables 30 and 31). The large decreases in alkalinity for both Metso 200 at 10 g/L and NaOH at 10 g/L were primarily due to dissolution and precipitation reactions rather than ion exchange.

8.3.5 Alkalinity Consumption

The alkali consumption by the core material in these experiments was significant. At 0.1 g alkali/L, essentially all the useful alkalinity was consumed. At concentrations of 10 g/L, 60.1-69.5% of the NaOH was consumed and 66.3-74.1% of the Metso 200, depending upon the pH used for comparison.

The alkali consumption values at 10 g/L concentrations of NaOH and Metso 200 were respectively 3.57-4.01 and 2.37-2.74 meq/100 g of core (Table 30). Due to the high solids/liquid

ratio (Section 8.2.2) and the fixed amount of alkali available, the maximum alkali consumption values that would be expected in these experiments if all the alkali was consumed are, 5.95 meq/100 g core for NaOH and 4.31 meq/100 g core for Metso 200.

Alkalinity consumption data are very dependent upon solid/liquid ratio, ω_s , used in the experiments and can vary by an order of magnitude. The alkalinity loss decreases as ω_s increases [56]. Thus, the values in this study may be minimums, since just enough liquid was used to fill the pore spaces and the solid/liquid ratio was approximately 5:1.

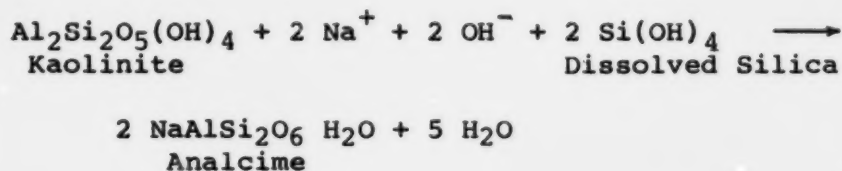
Several methods of determining and expressing caustic consumption are presented in the literature. For example, tests use widely varying solid/liquid ratios and also different end points for the alkalinity titration. Thus, the literature data cannot be readily compared [55]. Some standardization of methods, for example the use of specified solid/liquid ratios and the plotting of titration curves, would help in the comparison of results.

8.3.6 Preserved Core Floods

Effluents from the preserved core floods (Section 6.2) were analyzed for silicon and one sample from each run was analyzed for sodium and trace element composition. The effluent samples from the core were initially dissolved in tetrahydrofuran for the bitumen and water analyses required for Section 6.2. These tetrahydrofuran solutions were evaporated, ashed and dissolved in hydrochloric/hydrofluoric acids for determination of silicon and elemental composition by atomic absorption and plasma spectrometry. (For methods see Section 8.2.3.) The results were then calculated for the aqueous phase of the core effluent. Since the tetrahydrofuran solutions were not filtered, the results represent the total silicon and total metals, including contamination from the crude. The results should be interpreted on this basis. This work was done to gain some additional information from Section 6.2 and was not specifically designed to study alkali/rock interactions.

The total silicon analysis from the preserved core effluents for runs PC1, PC2, PC3 and PC4 are shown in Table 32 and the elemental composition of four samples in Table 33. Silicon and aluminum concentrations in the NaOH flood samples are higher than those of the brine, as would be expected based on

the leach results. However, in the flood experiments silicon and aluminum concentrations in the alkali effluent are an order of magnitude higher than those in the NaOH leach studies. These higher levels may be partly due to suspension of clays and fine silica in the core effluent (Table 34) or else they represent a stage in the alkali/rock interactions where lower amounts of the dissolved silicon and aluminum have been removed from solution by new mineral formation [55]. Many reactions occur during alkali/rock interactions which can remove silicon and aluminum (and also sodium) from solution. The following one, which produces analcime, is very common [55, 58]:



The largest change in elemental composition occurred in Run #4 using 10 g NaOH/L alkali flood in brine (Table 33). The initial sodium concentration was approximately 7620 mg/kg, but the core effluent contained only 1100 mg Na/kg. This is consistent with the decrease in sodium concentration found in the 10 g NaOH/L leach experiment and represents a very high level of caustic consumption. Further data on NaOH core floods, and especially Metso 200 floods, are needed to assess alkali consumption and formation damage.

8.3.7 Field Application

One of the critical chemical flood design parameters is alkali consumption. The literature indicates that, a concentration of alkali higher than that which produces minimum interfacial tension must be used if the alkaline bank is to propagate through the reservoir at an economically accepted rate [61]. Some studies have shown that low alkali concentration, e.g. 2 g/L, will not survive where there is a long residence time in the reservoir [62]. Other problems which can occur are damage at the injectors or producers due to precipitation/scale formation [63]. These operational problems can be minimized by proper design of the flood.

The data from the static tests described above and preserved core floods only identify the nature of the problem and further experiments are required to define the amount of caustic consumption that would be encountered in the field, and the impact of alkali on formation permeability.

The Conclusions/Recommendations section outlines some recommended studies which would better define caustic consumption and related problems. The data from these suggested experiments should aid in the design of a caustic flood which will have a higher probability of success in the field and fewer operational problems.

TABLE 23

ELEMENTAL ANALYSIS OF BRINE FROM
CONDITIONING OF CORE MATERIAL FOR TWO DAYS

(Results in mg/kg)

Co	<0.02
Zn	0.02
Cd	<0.02
B	0.80
Bi	<0.1
P	<0.1
Be	<0.005
Si	2.2
Fe	<0.02
Mn	0.02
Ca	40
Mg	15
Cu	0.03
Al	0.05
V	0.03
Mo	0.30
Pb	0.02
Ni	<0.02
Cr	<0.02
Na	2850
K	29.7

TABLE 24

ELEMENTAL ANALYSIS OF BRINE LEACHATE - 36 DAYS

(Results in mg/kg)

<u>Element</u>	<u>F2 Original</u>	<u>F2 Leach</u>
Co	<0.05	<0.05
Zn	<0.05	<0.05
Cd	<0.05	<0.05
B	<0.05	<u>0.74</u>
Bi	<0.1	<0.1
P	<0.5	<0.5
Be	<0.01	<0.01
Si	<0.1	<u>8.13</u>
Fe	0.20	<0.05
Mn	<0.05	0.67
Ca	0.07	<u>100</u>
Mg	<0.05	<u>25.6</u>
Cu	<0.05	<0.05
Al	0.19	<u>0.70</u>
V	<0.05	<0.05
Mo	<0.05	0.50
Pb	<0.05	0.06
Ni	<0.05	<0.05
Cr	<0.05	<0.05
Na	2000	2200
K	0.76	<u>30.1</u>

TABLE 25

ELEMENTAL ANALYSIS OF SODIUM HYDROXIDE LEACHATES - 36 DAYS

(Results in mg/kg)

	<u>F3 Original</u> <u>0.1 g NaOH/L</u>	<u>F3 Leach</u> <u>0.1 g NaOH/L</u>	<u>F4 Original</u> <u>10 g NaOH/L</u>	<u>F4 Leach</u> <u>10 g NaOH/L</u>
Co	<0.05	<0.05	<0.05	<0.05
Zn	<0.05	0.06	<0.05	0.08
Cd	<0.05	0.05	<0.05	<0.05
B	<0.05	<u>0.76</u>	<0.05	<u>1.32</u>
Bi	<0.1	<0.1	<0.1	0.1
P	<0.5	<0.5	<0.5	5.2
Be	<0.01	<0.01	<0.01	<0.01
Si	0.14	<u>9.87</u>	0.16	<u>172</u>
Fe	0.05	0.05	<0.05	0.84
Mn	<0.05	0.21	<0.05	<0.05
Ca	<0.05	<u>99.5</u>	0.33	<u>0.87</u>
Mg	<0.05	<u>8.14</u>	<0.05	<0.05
Cu	<0.05	0.05	<0.05	0.66
Al	0.16	0.24	<0.05	<u>74.4</u>
V	<0.05	<0.05	<0.05	1.31
Mo	<0.05	0.46	<0.05	0.35
Pb	<0.05	<0.05	<0.05	<0.05
Ni	<0.05	<0.05	<0.05	<0.05
Cr	<0.05	<0.05	<0.05	0.19
Na	1900	2200	7620	5400
K	0.81	<u>30.1</u>	<u>1.46</u>	<u>51.8</u>

TABLE 26

ELEMENTAL ANALYSIS OF METSO 200 IN LEACHATES - 36 DAYS

(Results in mg/kg)

	<u>F5 Original</u> <u>0.1 g METSO/L</u>	<u>F5 Leach</u> <u>0.1 g METSO/L</u>	<u>F6 Original</u> <u>10 g METSO/L</u>	<u>F6 Leach</u> <u>10 g METSO/L</u>
Co	<0.05	<0.05	<0.05	<0.05
Zn	<0.05	0.08	0.09	0.06
Cd	<0.05	<0.05	<0.05	<0.05
B	<0.05	<0.12	0.29	1.12
Bi	<0.1	<0.1	0.65	0.25
P	<0.5	<0.5	0.5	5.4
Be	<0.01	<0.01	<0.01	<0.01
Si	<u>12.9</u>	<u>11.6</u>	<u>1260</u>	<u>514</u>
Fe	1.10	<0.05	0.47	1.5
Mn	<0.05	0.61	<0.05	<0.05
Ca	<u>0.26</u>	<u>76.6</u>	<u>0.33</u>	<u>0.90</u>
Mg	<0.05	<u>17.4</u>	<u>0.16</u>	<u>0.33</u>
Cu	<0.05	<0.05	<0.05	0.83
Al	<u>0.20</u>	<u>0.37</u>	<u>1.42</u>	<u>8.35</u>
V	<0.05	<0.05	<0.05	0.88
Mo	<0.05	0.40	0.06	0.35
Pb	<0.05	<0.05	0.07	0.05
Ni	<0.05	<0.05	<0.05	<0.05
Cr	<0.05	<0.05	<0.05	0.06
Na	2000	2300	<u>6480</u>	<u>3980</u>
K	0.84	<u>22.5</u>	3.1	<u>31.0</u>

TABLE 27

ALKALI CONSUMPTION
TITRATION OF FLOOD BRINE AND BRINE LEACHATE

(10.0 g Sample)

<u>F2 Original</u>		<u>F2 Leach</u>	
pH	mL of 0.005 N HCl	pH	mL of 0.005 N HCl
4.16	0	7.41	0
		6.92	0.47
		6.75	0.71
		6.63	0.94
		6.45	1.41
		6.28	1.88
		6.15	2.35
		6.05	2.82
		5.95	3.29
		5.86	3.76
		5.77	4.23
		5.68	4.70
		5.59	5.17
		5.50	5.64
		5.38	6.11
		5.25	6.58
		5.08	7.05
		4.82	7.52
		4.67	7.71
		4.50	7.90
		4.26	8.08
		3.77	8.46
		3.16	9.40

FIGURE 37
TITRATION CURVES FOR
FLOOD BRINE AND LEACHATE

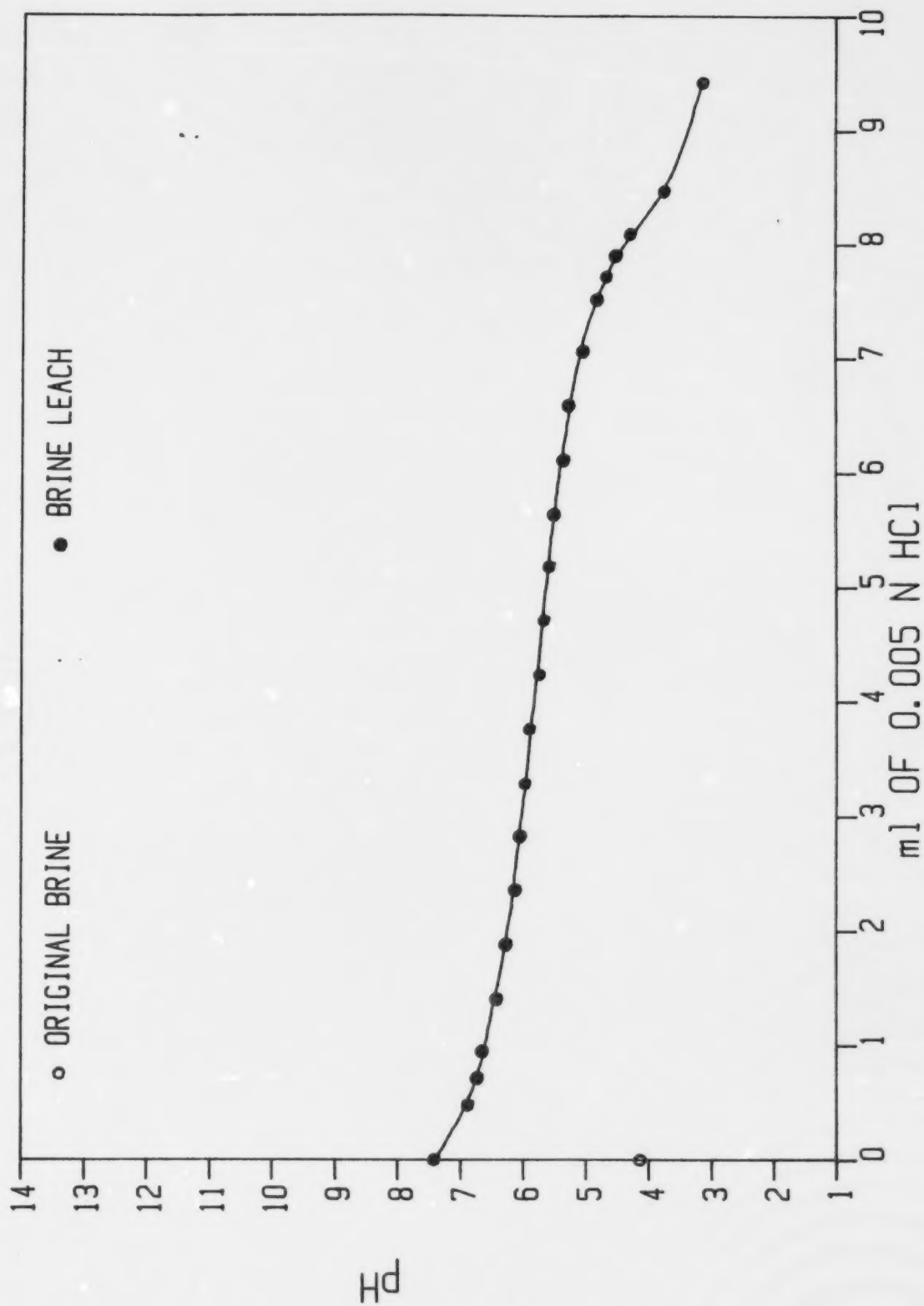


TABLE 28

ALKALI CONSUMPTION
TITRATION OF SODIUM HYDROXIDE SOLUTIONS AND LEACHATES

(10.0 g Samples)

<u>F3 Original</u>		<u>F3 Leach</u>		<u>F4 Original</u>		<u>F4 Leach</u>	
pH	mL of HCl 0.005 N	pH	mL of HCl 0.005 N	pH	mL of HCl 0.5 N	pH	mL of HCl 0.5 N
10.40	0	7.95	0	12.71	0	12.20	0
10.27	0.47	7.30	0.53	12.58	1.00	11.82	0.88
10.12	0.94	6.80	1.05	12.40	2.00	9.36	1.75
9.92	1.41	6.54	1.58	12.19	3.00	8.89	1.84
9.67	1.88	6.36	2.10	11.82	4.00	7.86	1.93
9.40	2.35	6.23	2.63	11.37	4.50	6.72	1.98
8.97	2.81	6.14	3.16	10.36	4.75	6.28	2.01
8.72	3.00	6.10	3.42	9.35	4.82	5.75	2.10
8.48	3.10	6.00	3.95	5.82	4.90	5.28	2.19
7.80	3.24	5.90	4.48	2.35	5.02	4.60	2.28
7.00	3.38	5.86	5.53	1.90	5.10	3.60	2.37
6.73	3.47	5.73	6.05			2.50	2.45
6.40	3.66	5.64	6.31			2.04	2.54
6.13	4.03	5.56	6.58				
5.85	4.22	5.48	6.84				
5.46	4.50	5.26	7.37				
4.96	4.78	4.97	7.90				
4.22	4.97	4.76	8.16				
3.93	5.07	3.97	8.69				
3.23	5.63	3.26	9.48				

FIGURE 38

TITRATION CURVES FOR F3
SODIUM HYDROXIDE SOLUTION
(0.1 G/L) AND LEACHATE

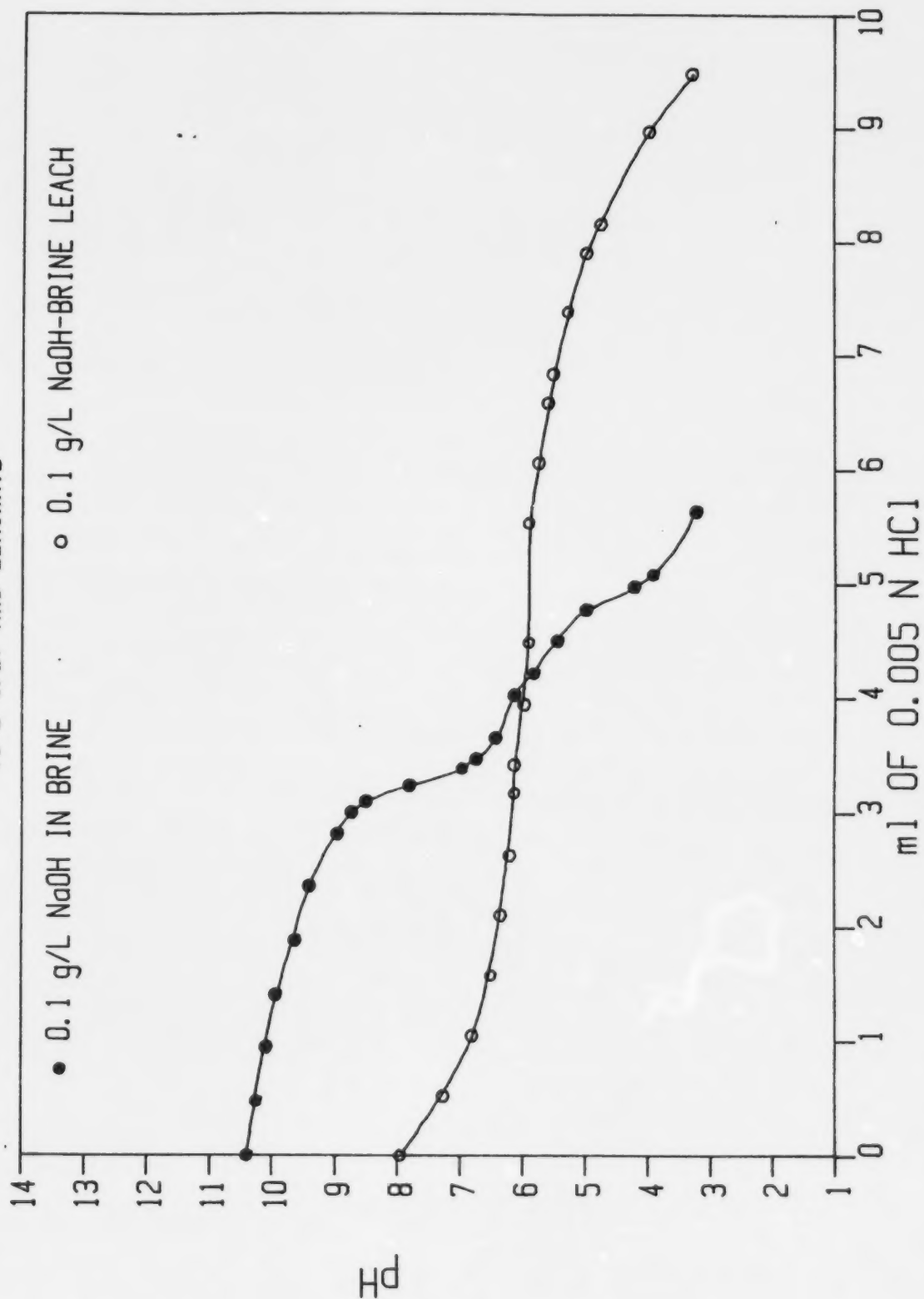


FIGURE 39
TITRATION CURVES FOR F4
SODIUM HYDROXIDE SOLUTION
(10 g/L) AND LEACHATE

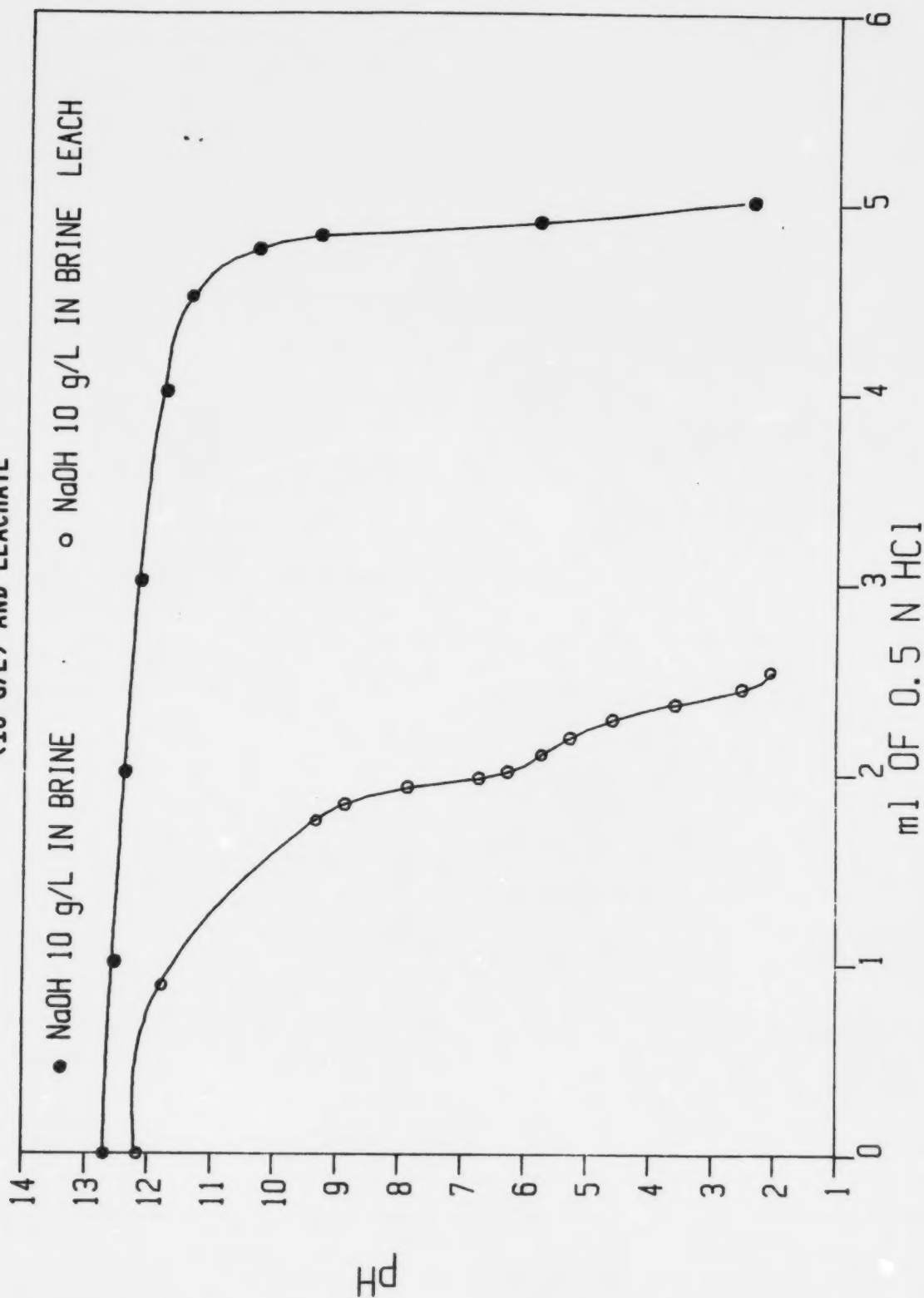


TABLE 29

ALKALI CONSUMPTION
TITRATION OF METSO 200 SOLUTIONS AND LEACHATES

(10.0 g Samples)

<u>F5 Original</u>		<u>F5 Leach</u>		<u>F6 Original</u>		<u>F6 Leach</u>	
pH	mL of HCl 0.005 N	pH	mL of HCl 0.005 N	pH	mL of HCl 0.5 N	pH	mL of HCl 0.5 N
10.54	0	7.54	0	12.34	0	11.64	0
10.42	0.43	7.26	0.19	12.19	0.90	11.07	0.49
10.30	0.85	7.03	0.38	11.91	1.80	9.07	0.99
10.13	1.28	6.84	0.57	10.98	2.71	8.60	1.09
9.90	1.70	6.58	0.94	10.71	2.80	8.33	1.18
9.63	2.13	6.44	1.22	10.20	2.98	7.10	1.28
9.24	2.55	6.35	1.51	10.00	3.07	6.16	1.33
8.68	2.98	6.22	1.89	9.32	3.34	5.82	1.38
8.45	3.06	6.13	2.26	8.75	3.52	5.48	1.43
8.09	3.15	6.07	2.64	8.30	3.61	5.68	1.48
7.16	3.23	5.92	3.30	7.26	3.70	3.73	1.53
5.92	3.40	5.81	3.77	2.90	3.79	2.32	1.58
5.68	3.49	5.71	4.24				
5.14	3.57	5.49	5.19				
4.40	3.66	5.01	6.60				
3.85	3.83	4.65	7.07				
3.30	4.26	4.00	7.54				
3.05	4.68	3.26	8.49				
2.93	5.11	3.00	9.43				

FIGURE 40

TITRATION CURVES FOR F5
METS0 200 SOLUTION
(0.1 g/L) AND LEACHATE

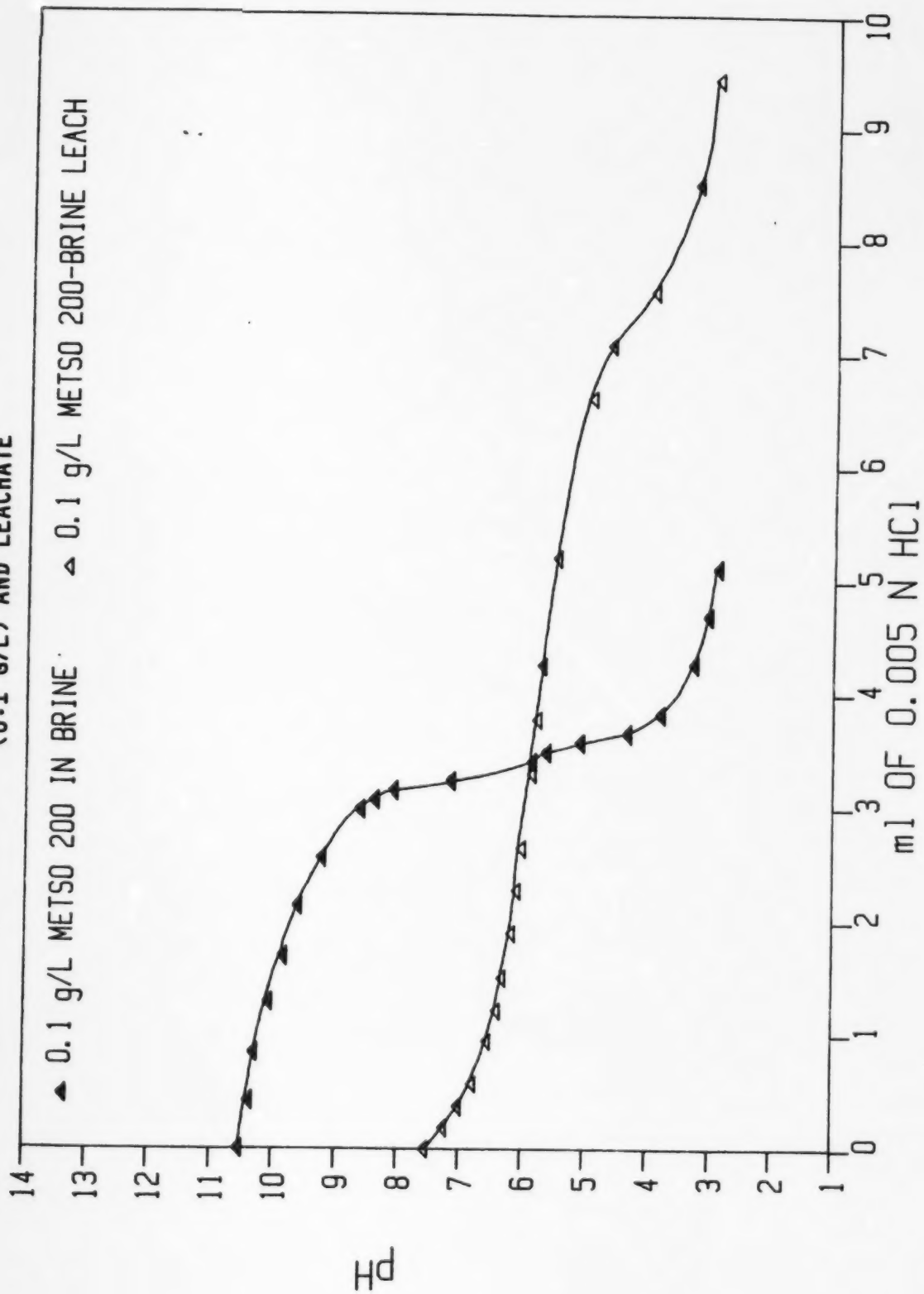


FIGURE 41
TITRATION CURVES FOR F6
METSO 200 SOLUTION
(10 g/L) AND LEACHATE

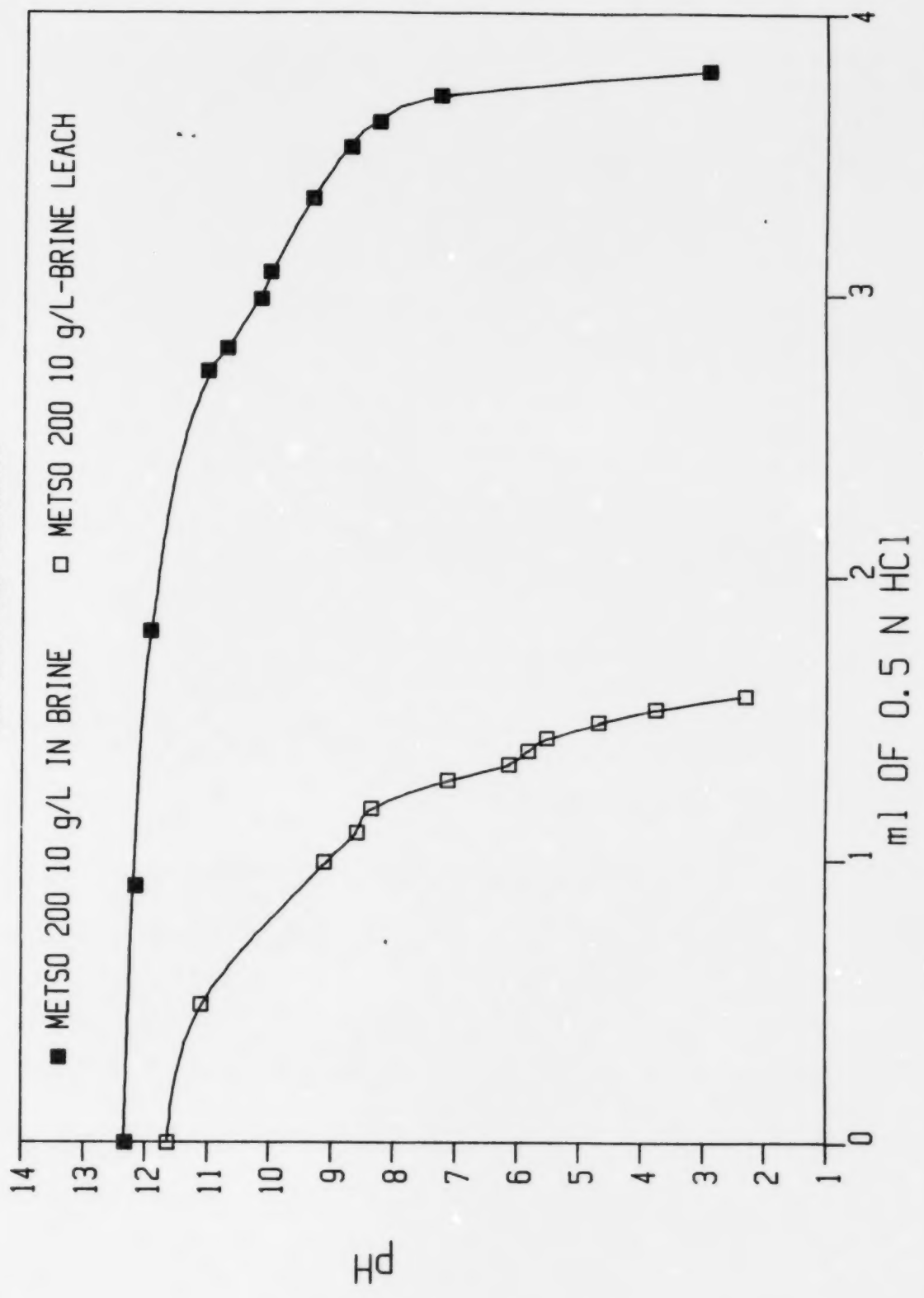


TABLE 30

ALKALI CONSUMPTION BY CORE MATERIAL
IN MILLIEQUIVALENTS PER 100 g OF CORE

	<u>F3</u>	<u>F4</u>	<u>F5</u>	<u>F6</u>
pH of Original Soln.	10.40	12.71	10.54	12.34
pH of Leach	7.95	12.20	7.54	11.64
Alkalinity Loss at Leach pH	0.0310	3.67	0.0347	2.37
Alkalinity Loss at pH 10.5	--	4.01	--	2.38
Alkalinity Loss at pH 8.3	--	3.60	--	2.72
Alkalinity Loss at pH 7.6	0.0288(a)	3.57	0.0347	2.74
Total Alkalinity of Initial Brine/Core Mix (to pH 7.6)	0.0318(b)	5.95 (b)	0.0347 (b)	4.13 (b)

(a) Value is low due to buffering from dissolved components from the core. It is unlikely that any "effective" alkalinity remains.

(b) Maximum alkali consumption in meq/100 g core that could be obtained under experimental conditions, i.e. consumption of all caustic from liquid phase.

TABLE 31

ALKALI CONSUMPTION
IN PERCENT

	<u>F3</u>	<u>F4</u>	<u>F5</u>	<u>F6</u>
pH of Leach	7.95	12.20	7.54	11.64
Alkalinity Loss at pH 10.5 (%)	--	69.5	100	74.1
Alkalinity Loss at pH 8.3 (%)	100	60.7	100	67.3
Alkalinity Loss at pH 7.6 (%)	90.8(a)	60.1	100	66.3

$$\% \text{ Loss in Alkalinity} = \frac{V_1 - V_2}{V_1} \times 100\%$$

where V_1 = mL of titrant for 10 g of original solution
 V_2 = mL of titrant for 10 g of leachate solution

(a) Value is low due to buffering from dissolved components from the core. It is unlikely that any "effective" alkalinity remains.

TABLE 32

CALCULATED CONCENTRATION OF SILICON IN THE AQUEOUS PHASE
OF PRESERVED CORE EFFLUENTS

(Results in mg/kg)

Sample #	Run PC1 Brine	Run PC3 pH 8.5 NaOH in Brine	Run PC4 10 g/L NaOH in Brine	Run PC5 0.1 g/L NaOH in Brine
1	9.28	--	--	--
2	7.62	28.1	638	117
3	5.89	12.3	171	175
4	5.01	10.7	111	670
5	2.38(a)	21.1	6.08(a)	222
6	1.53	51.6(a)	303	195
7	<1	97.0	42	121(a)
8	1.93	62.8	141	113
9	1.53	32.1	10	168
10	--	23.2	23	64
11	--	13.3	--	47
12	--	--	--	39

(a) Trace element analysis given in Table 33

TABLE 33

CALCULATED CONCENTRATION OF TRACE ELEMENTS IN THE AQUEOUS PHASE
OF PRESERVED CORE EFFLUENTS

(Results in mg/kg)

Element	Run #1-5 Brine	Run #3-6 0.1 g/L NaOH in Brine	Run #4-5 10 g/L NaOH in Brine	Run #5-7 0.1 g/L NaOH in Brine
Co	<0.3	<0.3	<0.3	<0.3
Zn	13.8	0.27	0.46	0.96
Cd	<0.3	<0.3	<0.3	<0.3
B	<0.3	<0.3	<0.3	<0.3
Bi	<2	<2	<2	<2
P	<2	<2	<2	<2
Be	<0.1	<0.1	<0.1	<0.1
Si	<1	46.1	9.44	129
Fe	8.77	6.64	4.27	19.2
Mn	<0.3	<0.3	<0.3	0.27
Ca	7.77	2.30	<2	2.88
Mg	6.64	2.17	0.69	3.98
Cu	<0.3	<0.3	0.38	<0.3
Al	1.25	19.0	8.25	57.6
V	6.01	5.15	2.89	4.52
Mo	<0.3	0.03	<0.3	<0.3
Pb	4.51	<0.3	<0.3	<0.3
Ni	2.00	0.41	1.22	1.37
Cr	<0.3	<0.3	0.30	<0.3
Na	2794	1880	1100(a)	2020
K	12.3	8.13	2.13	12.1

(a) Sodium has been depleted from injected alkali

TABLE 34

SIEVE ANALYSIS OF EDAM CORE
WELL # 9C-24-48-21-W3M

<u>Sample Retained on</u>	<u>Sample 1 wt. %</u>	<u>Sample 2 wt. %</u>
40 mesh	0.33	0.25
80 mesh	23.21	30.68
100 mesh	37.66	33.70
200 mesh	36.15	32.62
250 mesh	0.65	0.78
Pass 250 mesh	2.00	1.98

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APPENDIX A

SYNTHETIC CORE DISPLACEMENT TABLES

Table A1

RUN # 133-1

Distilled water at 182 g/h

SAMPLE No.	Time (s)	Feed scale (g)	Total product (g)	Water produced (g)
1	0.00	2475.00	0.00	0.00
2	300.00	2460.00	0.86	0.00
3	600.00	2444.00	14.52	1.20
4	900.00	2429.00	15.62	7.42
5	1500.00	2397.00	31.35	28.54
6	2400.00	2349.00	47.13	44.58
7	3600.00	2289.00	61.57	58.60
8	5600.00	2183.00	104.63	100.56
9	7200.00	2100.00	83.20	80.00
10	10600.00	1924.00	175.37	171.00
11	14700.00	1719.00	205.72	202.32
12	18400.00	1534.00	184.40	180.50
13	21800.00	1371.00	162.35	159.84

Table A2

RUN # 133-2

Brine at 199 g/h

SAMPLE No.	Time (s)	Feed scale (g)	Total product (g)	Water produced (g)
1	0.00	2597.10	0.00	0.00
2	100.00	2582.20	0.00	0.00
3	600.00	2566.60	15.07	1.40
4	900.00	2550.90	15.46	7.70
5	1200.00	2535.00	15.91	14.29
6	1800.00	2504.50	30.27	28.14
7	2700.00	2477.00	29.34	25.53
8	4500.00	2416.00	60.10	57.77
9	6600.00	2304.00	111.09	106.61
10	10600.00	2099.00	206.08	200.75
11	14600.00	1904.00	192.96	188.38
12	17300.00	1720.50	182.83	179.91
13	19300.00	1585.50	135.20	132.62

Table A7

RUN # 100-E

0.1 g/L NaOH at 187 g/h

SAMPLE No.	Time (s)	Feed scale (g)	Total product (g)	Water produced (g)
1	0.00	2459.70	0.00	0.00
2	100.00	2444.70	1.27	0.00
3	600.00	2429.40	15.14	1.40
4	900.00	2414.00	15.45	9.12
5	1200.00	2398.00	15.73	11.32
6	1800.00	2367.00	10.75	24.72
7	2700.00	2319.80	46.70	37.28
8	4200.00	2240.00	79.31	57.84
9	7000.00	2094.00	146.02	141.02
10	10400.00	1925.50	168.29	164.38
11	14000.00	1746.80	179.70	176.02

Table A4

RUN # 137-a

0.1 g/L NaOH at 282 g/h

SAMPLE No.	Time (s)	Feed scale (g)	Total product (g)	Water produced (g)
1	0.00	2945.40	0.00	0.00
2	100.00	2923.70	4.86	0.00
3	200.00	2902.50	20.11	0.80
4	300.00	2880.30	21.36	0.50
5	400.00	2857.00	23.07	10.00
6	500.00	2810.20	47.57	46.74
7	600.00	2763.20	47.34	44.74
8	700.00	2621.60	142.11	139.73
9	800.00	2440.80	180.47	177.68
10	900.00	2267.30	173.30	168.98
11	11280.00	2063.60	203.71	200.58
12	13800.00	1864.20	198.18	195.70

Table AE

RUN # 133-7

10.0 g/L NaOH at 159 g/h

SAMPLE No.	Time (s)	Feed scale (g)	Total product (g)	Water produced (g)
1	0.00	3906.60	0.00	0.00
2	300.00	3891.60	1.75	0.00
3	600.00	3876.10	15.25	2.40
4	900.00	3860.40	15.20	0.63
5	1200.00	3844.30	15.66	6.96
6	1500.00	3828.20	15.92	13.73
7	2700.00	3764.20	63.95	59.89
8	4000.00	3694.70	69.30	66.72
9	5600.00	3609.00	95.30	91.78
10	8200.00	3506.50	102.80	99.16
11	12200.00	3430.00	76.09	72.74
12	16000.00	3230.00	199.26	193.77
13	19600.00	3043.70	186.58	182.06

Table Aa

RUN # 133-8

10.0 g/L NaOH at 269 g/n

SAMPLE No.	Time (s)	Feed scale (g)	Total product (g)	Water produced (g)
1	0.00	2741.80	0.00	0.00
2	300.00	2720.20	3.75	0.00
3	500.00	2697.60	22.28	0.90
4	900.00	2673.90	23.06	8.45
5	1200.00	2650.10	23.62	20.46
6	1800.00	2602.00	48.52	45.50
7	2400.00	2555.00	47.57	44.59
8	4280.00	2426.50	127.51	121.54
9	5500.00	2293.10	133.70	129.36
10	8700.00	2117.10	175.63	170.61
11	11300.00	1940.70	176.44	171.78
12	13406.00	1740.00	199.58	197.18

Table A7

RUN # 133-9

0.1 g/L METSO at 170 g/h

SAMPLE No.	Time (s)	Feed scale (g)	Total product (g)	Water produced (g)
1	0.00	1694.30	0.00	0.00
2	100.00	1679.90	1.43	0.00
3	600.00	1665.10	12.15	2.74
4	900.00	1650.70	14.26	3.72
5	1200.00	1635.90	14.75	10.80
6	1800.00	1606.60	28.91	23.81
7	2700.00	1562.50	44.15	35.77
8	4200.00	1489.50	72.20	60.47
9	7000.00	1360.00	129.28	122.97
10	9900.00	1235.00	124.35	120.51
11	13000.00	1080.00	154.79	150.97
12	16800.00	900.00	179.87	176.51
13	17800.00	851.50	48.79	47.65

Table A8

RUN # 133-10

0.1 g/L METSO 200 at 293 g/h

SAMPLE No.	Time (s)	Feed scale (g)	Total product (g)	Water produced (g)
1	0.00	1234.70	0.00	0.00
2	300.00	1212.50	2.67	0.00
3	600.00	1189.00	23.32	2.00
4	900.00	1165.40	23.58	20.12
5	1200.00	1141.80	23.61	21.87
6	1500.00	1094.40	47.09	44.42
7	2500.00	1015.30	79.17	75.17
8	4500.00	383.80	131.07	127.72
9	6500.00	725.50	157.19	153.19
10	8700.00	551.00	174.32	170.46
11	11100.00	364.00	188.09	184.67
12	13500.00	174.40	188.62	185.07

Table A^c

RUN # 133-11

10.0 g/L METSO 200 at 179 g/h

SAMPLE No.	Time (s)	Feed scale (g)	Total product (g)	Water produced (g)
1	0.00	3626.90	0.00	0.00
2	300.00	3612.40	1.26	0.00
3	600.00	3598.10	13.84	1.90
4	900.00	3582.60	15.16	2.48
5	1200.00	3569.00	13.19	4.21
6	1800.00	3539.10	29.91	25.34
7	2700.00	3494.40	45.73	43.02
8	4200.00	3420.10	73.96	70.70
9	6000.00	3352.50	67.76	65.71
10	8000.00	3236.70	115.16	110.90
11	11900.00	3047.40	189.33	183.86
12	16200.00	2922.60	223.45	217.04

Table A 10

RUN # 133-12

10.0 g/L METSO 200 at 289 g/h

SAMPLE No.	Time (s)	Feed scale (g)	Total product (g)	Water produced (g)
1	0.00	1876.20	0.00	0.00
2	300.00	1853.50	3.99	0.00
3	600.00	1830.10	23.04	2.57
4	900.00	1806.30	24.14	10.12
5	1200.00	1782.90	23.37	21.30
6	1500.00	1741.00	41.76	38.68
7	2700.00	1695.70	41.62	40.79
8	4500.00	1556.00	139.20	131.67
9	6400.00	1413.00	143.39	138.59
10	8200.00	1277.30	136.25	132.04
11	9600.00	1095.90	180.62	174.91
12	12100.00	905.30	189.18	184.38

Table A 11

RUN # 133-21

Distilled water at 178 g/h

SAMPLE No.	Time (s)	Feed scale (g)	Total product (g)	Water produced (g)
1	0.00	2312.70	0.00	0.00
2	300.00	2298.40	0.00	0.00
3	600.00	2283.70	14.56	2.55
4	900.00	2268.60	14.86	1.30
5	1200.00	2253.50	15.00	10.73
6	1800.00	2223.40	30.60	28.44
7	2400.00	2193.10	30.06	27.68
8	4200.00	2104.10	88.92	84.24
9	5900.00	1967.20	136.90	132.71
10	9900.00	1817.00	150.00	146.67
11	13650.00	1627.90	188.78	185.54
12	18450.00	1399.70	227.60	224.06

Table A 12

RUN # 133-22

Brine solution at 183 g/h

SAMPLE No.	Time (s)	Feed scale (g)	Total product (g)	Water produced (g)
1	0.00	2940.90	0.00	0.00
2	300.00	2926.50	0.00	0.00
3	600.00	2911.60	14.26	2.00
4	900.00	2896.30	16.44	1.00
5	1200.00	2881.20	15.21	9.70
6	1800.00	2850.40	30.50	27.39
7	2400.00	2819.90	30.45	28.38
8	4200.00	2728.40	91.27	86.68
9	6900.00	2590.90	137.37	132.50
10	10000.00	2433.50	157.06	153.08
11	14000.00	2230.00	203.16	198.34
12	18000.00	2028.00	201.56	197.96
13				

Table A 13

RUN # 133-27

Brine solution at 277 g/h

SAMPLE No.	Time (s)	Feed scale (g)	Total product (g)	Water produced (g)
1	0.00	2875.90	0.00	0.00
2	300.00	2854.00	7.26	0.00
3	600.00	2830.80	21.74	0.33
4	900.00	2807.60	23.05	17.73
5	1200.00	2784.30	23.28	22.20
6	1500.00	2737.60	46.48	44.59
7	2400.00	2691.10	46.43	44.63
8	4200.00	2551.60	139.57	134.61
9	6600.00	2366.90	184.51	179.42
10	9500.00	2141.70	224.80	220.89
11	12500.00	1914.40	227.02	221.62
12	15500.00	1685.30	229.63	225.39

Table A 14

RUN # 133-24

0.1 g/L NaOH at 172 g/h

SAMPLE No.	Time (s)	Feed scale (g)	Total product (g)	Water produced (g)
1	0.00	1948.70	0.00	0.00
2	300.00	1835.40	0.00	0.00
3	600.00	1821.60	12.82	3.50
4	900.00	1807.00	14.23	0.20
5	1200.00	1792.40	14.69	2.21
6	1800.00	1762.50	29.57	21.23
7	2400.00	1732.20	30.40	23.38
8	4200.00	1642.00	89.30	79.77
9	5400.00	1532.00	109.51	105.68
10	10200.00	1343.70	187.44	184.80
11	14300.00	1140.40	202.81	201.54
12	18000.00	957.20	192.45	180.95

Table A 15
RUN # 133-25

0.1 g/L NaOH at 278 g/h

SAMPLE No.	Time (s)	Feed scale (g)	Total product (g)	Water produced (g)
1	0.00	3560.90	0.00	0.00
2	200.00	3546.00	0.58	0.00
3	600.00	3515.70	29.52	1.49
4	900.00	3493.00	23.02	8.05
5	1200.00	3470.00	23.27	16.01
6	1800.00	3424.90	44.18	38.07
7	2400.00	3381.00	43.86	39.58
8	4200.00	3253.90	126.22	122.73
9	6400.00	3084.20	169.43	165.77
10	9000.00	2880.00	203.45	199.81
11	11600.00	2669.30	210.01	206.86
12	14200.00	2465.00	202.27	199.79

Table A 16

RUN # 133-26

10.0 g/L NaOH at 183 g/h

SAMPLE No.	Time (s)	Feed scale (g)	Total product (g)	Water produced (g)
1	0.00	3524.60	0.00	0.00
2	300.00	3511.50	0.00	0.00
3	600.00	3497.10	13.35	3.50
4	900.00	3482.50	14.43	0.20
5	1200.00	3467.30	14.79	2.65
6	1800.00	3436.90	30.21	24.19
7	2400.00	3406.40	30.50	26.29
8	4200.00	3314.20	92.36	87.16
9	6400.00	3201.40	112.95	107.81
10	10200.00	3007.20	193.83	187.33
11	14500.00	2787.50	219.22	212.84
12	19000.00	2557.60	229.17	222.63

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Table A 17

RUN # 133-27

10.0 g/L NaOH at 283 g/h

SAMPLE No.	Time (s)	Feed scale (g)	Total product (g)	Water produced (g)
1	0.00	2156.80	0.00	0.00
2	300.00	2174.20	7.29	0.00
3	600.00	2110.90	22.73	0.40
4	900.00	2087.10	23.79	11.19
5	1200.00	2063.30	24.04	21.27
6	1500.00	2016.00	46.75	43.56
7	2400.00	1968.70	47.14	45.22
8	4200.00	1827.00	141.35	175.66
9	5400.00	1654.00	172.86	167.31
10	8000.00	1451.20	202.39	196.45
11	12170.00	1201.10	249.43	240.61
12	15320.00	953.00	247.71	243.70

Table A 19

RUN # 173-28

0.1 g/L METSD 200 at 186 g/h

SAMPLE No.	Time (s)	Feed scale (g)	Total product (g)	Water produced (g)
1	0.00	1421.10	0.00	0.00
2	300.00	1406.60	0.54	0.00
3	600.00	1391.90	14.47	0.90
4	900.00	1376.50	15.23	0.50
5	1200.00	1361.10	15.25	7.99
6	1500.00	1330.20	10.76	23.61
7	1800.00	1319.10	10.54	25.20
8	4200.00	1206.50	92.56	83.36
9	6400.00	1091.00	113.02	106.94
10	10000.00	9907.20	195.63	181.95
11	13600.00	8720.20	186.33	184.21
12	17200.00	2533.90	186.90	185.27

Table A 19

RUN # 133-29

0.1 g/L METSO 200 at 276 g/h

SAMPLE No.	Time (s)	Feed scale (g)	Total product (g)	Water produced (g)
1	0.00	2131.90	0.00	0.00
2	300.00	2110.00	7.19	0.00
3	500.00	2094.50	15.76	0.26
4	900.00	2063.80	29.97	15.56
5	1200.00	2040.50	23.15	19.00
6	1800.00	1994.10	46.27	38.00
7	2400.00	1949.00	45.27	40.44
8	4200.00	1810.10	138.92	134.87
9	6400.00	1639.30	170.24	167.57
10	8200.00	1421.70	217.80	213.09
11	12200.00	1194.80	226.98	223.34
12	15500.00	943.80	249.33	245.95

Table A 20

RUN # 133-30

10.0 g/L METSO 200 at 184 g/h

SAMPLE No.	Time (s)	Feed scale (g)	Total product (g)	Water produced (g)
1	0.00	1298.00	0.00	0.00
2	300.00	1283.70	0.00	0.00
3	600.00	1269.00	13.83	1.00
4	900.00	1253.80	14.97	0.10
5	1200.00	1238.50	14.76	2.83
6	1800.00	1207.90	30.37	25.11
7	2400.00	1176.90	30.70	28.25
8	4200.00	1084.40	91.28	87.21
9	6400.00	971.70	111.75	106.65
10	10000.00	787.00	182.84	174.13
11	14000.00	582.90	202.57	196.05
12	18700.00	342.90	238.09	230.99

Table A 21

RUN # 133-31

10.0 g/L METSO 200 at 283 g/h

SAMPLE No.	Time (s)	Feed scale (g)	Total product (g)	Water produced (g)
1	0.00	2495.50	0.00	0.00
2	300.00	2473.20	8.38	0.00
3	600.00	2450.00	22.86	0.30
4	900.00	2426.50	23.20	9.85
5	1200.00	2402.90	23.60	20.39
6	1800.00	2355.90	46.96	42.10
7	2400.00	2308.30	47.00	43.85
8	4400.00	2151.10	155.76	149.23
9	7200.00	1930.70	218.42	210.39
10	10000.00	1709.90	219.44	212.79
11	12800.00	1489.90	217.70	211.07

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APPENDIX B

PRESERVED CORE DISPLACEMENT TABLES

Table B1

RUN # PC 1

Total sample weight (g)	% oil	% water	Norm. cumulative oil (g)	Norm. cumulative water (g)
6.69	38.50	60.90	2.59	4.10
8.17	13.40	83.50	3.72	11.14
5.90	10.10	88.70	4.32	16.44
11.61	6.10	91.90	5.05	27.32
19.34	3.50	94.90	5.73	45.98
24.69	2.10	96.50	6.26	70.14
20.66	2.00	100.70	6.66	90.40
21.95	1.70	97.40	7.04	111.97
27.68	1.50	96.40	7.46	139.23

PV = 25.0 ml

HCPV = 22.95 ml

Permeability = -----

Porosity = 0.38

Table B2

RUN # PC 2

Total sample weight (g)	% oil	% water	Norm. cumulative oil (g)	Norm. cumulative water, (g)
1.03	112.40	2.40	1.01	0.02
5.83	35.40	64.90	3.07	3.79
6.77	16.00	85.50	4.13	9.50
10.07	9.10	91.10	5.05	18.65
16.27	5.80	94.90	5.98	33.99
19.91	4.10	96.60	6.80	53.08
19.94	3.50	98.00	7.48	72.34
26.30	2.20	97.60	8.06	98.06
26.53	1.50	98.60	8.46	124.19
32.60	1.30	100.80	8.88	156.37
38.64	0.90	100.70	9.22	194.67

PV = 27.87 ml

HCPV = 21.44 ml

Permeability = 0.52 Darcy

Porosity = 0.44

Table B3

RUN # PC 3

Total sample weight (g)	% oil	% water	Norm. cumulative oil (g)	Norm. cumulative water (g)
2.90	102.40	0.00	2.90	0.00
6.41	47.20	52.70	5.93	3.38
6.41	12.70	83.80	6.77	8.95
10.20	5.30	88.40	7.35	18.57
10.25	2.80	90.20	7.66	28.51
17.08	2.70	97.30	8.12	45.13
19.73	1.80	95.20	8.49	64.49
22.00	1.40	98.60	8.80	86.18
44.00	1.10	92.10	9.31	129.67
31.20	0.50	99.50	9.47	160.71

PV = 29.95 ml

HCPV = 21.98 ml

Permeability = 0.74 Darcy

Porosity = 0.44

Table B4

RUN # PC 4

Total sample weight (g)	% oil	% water	Norm. cumulative oil (g)	Norm. cumulative water (g)
0.30	98.00	2.00	0.29	0.01
5.85	73.20	31.10	4.40	1.75
7.65	34.10	64.00	7.06	6.74
2.37	35.10	67.60	7.87	8.30
6.41	17.00	82.50	8.96	13.62
9.13	6.50	94.40	9.55	22.16
12.27	3.80	93.80	10.03	33.95
9.77	3.60	98.10	10.38	43.37
21.29	6.00	93.10	11.66	63.38
27.66	0.10	100.80	11.69	91.01
25.86	0.80	101.40	11.89	116.67
38.75	0.30	100.30	12.01	155.30

PV = 21.68 ml

HCPV = 19.20 ml

Permeability = 2.25 Darcy

Porosity = 0.36

Table 25

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RUN # FC 5

Total sample weight (g)	% oil	% water	Norm. cumulative oil (g)	Norm. cumulative water (g)
4.14	76.00	28.40	3.01	1.13
5.53	26.70	73.10	4.49	5.18
5.68	15.20	86.80	5.34	10.01
6.18	10.80	89.70	6.00	15.53
11.44	6.80	95.30	6.77	26.20
17.33	5.10	95.90	7.64	42.66
17.84	4.60	96.20	8.45	59.69
21.24	3.40	98.60	9.16	80.22
27.13	3.10	98.60	9.98	106.53
31.53	2.80	100.80	10.84	137.20
4.01	18.80	93.20	11.58	140.47
3.62	3.70	99.40	11.71	143.96
5.89	16.70	97.60	12.65	148.91
5.98	14.60	91.30	13.47	154.07
6.05	11.70	93.30	14.15	159.44
6.27	10.60	93.60	14.79	165.07
12.50	5.40	97.10	15.44	176.92
11.60	4.10	97.30	15.91	188.05
19.28	2.90	95.00	26.48	206.76
16.18	1.80	100.30	16.77	222.65
20.59	1.10	100.60	16.99	243.02
23.60	1.40	101.60	17.31	266.30

PV = 23.53 ml

HCPV = 21.52 ml

Permeability = 1.90 Darcy

Porosity = 0.35